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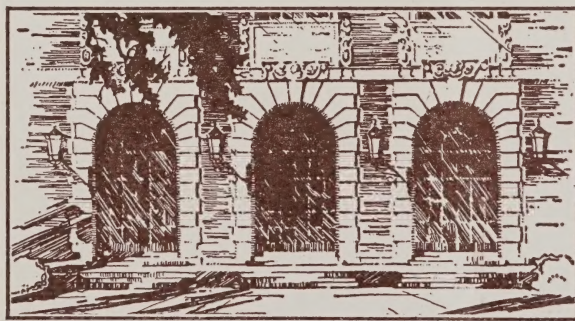
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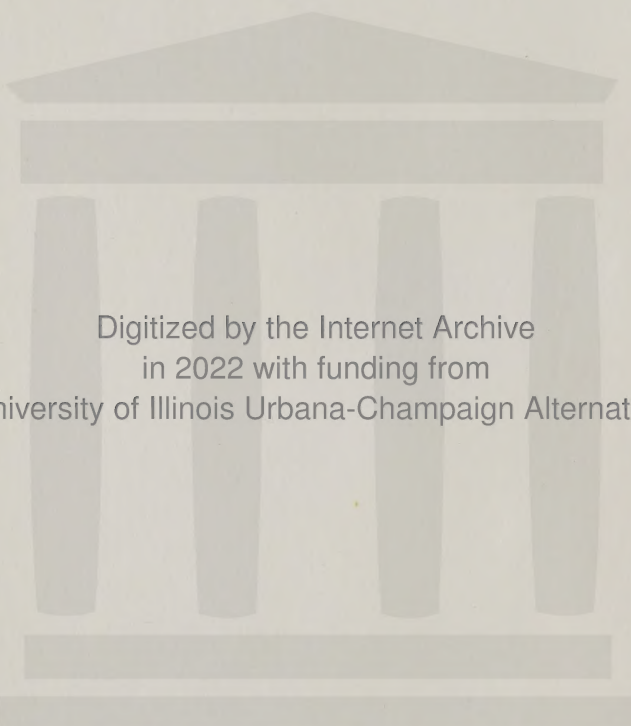
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TRANSACTIONS.

I.—*Influence of Temperature on the Refractive Power and on the Refraction Equivalents of Acetylacetone and of Ortho- and Para-toluidine.*

By W. H. PERKIN, Ph.D., F.R.S.

IN 1892, I communicated to the Society a description of an apparatus for determining the refractive power of compounds at different temperatures, together with some results obtained by its use (Trans., 1892, **61**, 287). In two later communications, an account was given of the magnetic rotation of substances supposed to contain acetyl, or to be of ketonic origin (Trans., 1892, **61**, 800, and 1894, **65**, 815); in these it was shown, from their magnetic rotations, that some di- and tri-ketonic compounds are tautomeric, and that when heated they change in varying degrees from their hydroxylic, or unsaturated form, to their saturated, or ketonic form, the rotations becoming lower in consequence. The refractive power of several of these compounds was also taken at different temperatures, showing changes in reference to this property, of the same order as in the case of the rotations; this was expected because it has been shown (Gladstone and Perkin, Trans., 1889, **55**, 750) that there is an analogy in most cases between the variations in the rotation and refraction of the same compounds.

Among the substances examined, acetylacetone, methylacetylacetone, allylacetylacetone, and diacetylacetone were shown to undergo internal change, in the most striking manner, by change of temperature.

Since the account of these experiments was published, Brühl, in his
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interesting paper entitled a "Study of Tautomerism," gives the results he obtained on the refractive power of acetylacetone at temperatures wide apart; the numbers, however, do not agree with mine, and the same is the case with some of his more recent measurements of the refractive power of para- and ortho-toluidines (*Zeit. phys. Chem.*, 1895, **16**, 216). Knowing the great care Professor Brühl takes in making his determinations, I have been induced to repeat my measurements of acetylacetone and the two toluidines, to see if any error could be discovered in the previous work, or any other explanation found of these discrepancies, for it is of great importance from a theoretical point of view to find out whether the analogy between the refraction and magnetic rotation of the di- and triketonic and other compounds, which my results are supposed to indicate, exists or not.

In all my determinations, I have used the apparatus described in this Journal a few years ago (*Trans.*, 1892, **61**, 288), which is simply a hollow prism containing the substance under examination, heated in an air bath. In making the observations, readings were invariably taken from both sides of the prism, and the sum of the result divided by two, so that if any slight shifting of the zero took place during the raising of the temperature (which, however, does not appear to occur) it would not influence the result.

I understand from Professor Brühl that in his determinations of the refractive power of acetylacetone, and I presume also in that of the toluidines and other substances, where temperatures above that of the atmosphere are employed, he used the total refractometer which he has described (*Ber.*, 1891, **24**, 286).

The following results were obtained with acetylacetone. The specimen employed was that given to me by Professor Claisen, and referred to in the Transactions (1892, **61**, 844) as Specimen II. The first set of results marked "A," given below, were made some time since, the product being previously distilled under the ordinary pressure. The other three, marked "B," were obtained quite recently; for these the acetylacetone was redistilled under reduced pressure the day before it was examined, and, as the specimens were not quite identical, the results have been kept separate. For the purposes of this paper it will only be necessary to give the numbers for the three hydrogen lines.

A.			B.				
Line	$t.$		$t.$		$t.$	$t.$	
H $_{\alpha}$	15.5°	1.44930.	6.5°	1.45459.	8°	1.45390.	9.5° 1.45270.
H $_{\beta}$	15.5°	1.46718.	6.5°	1.47259.	8°	1.47200.	9.5° 1.47053.
H $_{\gamma}$	15.5°	1.47939.	6.5°	1.48524.	8°	1.48451.	9.5° 1.48315.

Densities—

“A.” $d_{15.5^\circ/4^\circ}$ 0.9800.“B.” $d_{6.5^\circ/4^\circ}$ 0.9871. $d_{8^\circ/4^\circ}$ 0.9862. $d_{9.5^\circ/4^\circ}$ 0.9827.Molecular refraction $\frac{\mu - 1}{d} p$.

A.

B.

H_α	15.5°	45.807.	6.5°	46.041.	8°	46.026.	9.5°	46.060.
H_β	15.5°	47.629.	6.5°	47.874.	8°	47.861.	9.5°	47.871.
H_γ	15.5°	48.875.	6.5°	49.155.	8°	49.129.	9.5°	49.167.

The following are the results obtained at higher temperatures.

A.

B.

H_α	99.2°	1.40210.	99.0°	1.40240.
H_β	99.2°	1.41604.	99.0°	1.41656.
H_γ	99.2°	1.42555.	99.0°	1.42605.

Densities—

 $d_{99.2^\circ/4^\circ}$ 0.8975. $d_{99^\circ/4^\circ}$ 0.8960.Molecular refraction $\frac{\mu - 1}{d} p$.

A.

B.

H_α	99.2°	44.802.	99°	44.908.
H_β	92.2°	46.355.	99°	46.488.
H_γ	99.2°	47.415.	99°	46.547.

Relationship of Results.

A.

15.5°	H_α	45.807.	H_β	47.629.	H_γ	48.875.
99.2°	H_α	44.802.	H_β	46.355.	H_γ	47.415.
Diff.	83.7	1.005	1.274	1.460		

B.

Av. 8°	H_α	46.042.	H_β	47.869.	H_γ	49.150.
99°	H_α	44.908.	H_β	46.488.	H_γ	47.547.
Diff.	91°	1.134	1.381	1.603		

The results already published, obtained by the examination of the acetylacetone, given to me by Professor Dunstan (Trans., 1892, 61, 840, 847), called “Specimen I,” although represented by slightly lower numbers than those given above, exhibited very similar differences for variations of temperature. For 88.3° they are 1.103,

1.341, 1.551 respectively, these and the above calculated for 100°, give—

	H _α .	H _β .	H _γ .
A	1.200	1.522	1.744
B	1.246	1.517	1.761
Spec. I....	1.249	1.518	1.756
<hr/>			
Average diff.	1.232	1.519	1.754

These differences are as close to each other as could be expected, and show that the results obtained with my instrument are very regular; these vary, however, with the line taken for comparison, that for H_γ being considerably larger than that for H_α, showing that the *dispersion* as well as the refraction diminishes with rise of temperature.

The fresh results given above are therefore seen to be in close agreement with those previously published.

The numbers obtained by Brühl for acetylacetone (*J. pr. Chem.*, 1894, **50**, 190), and compared with the above, corrected for temperature by the coefficient 1.232 for 100°, are as follows.

	Brühl.	Perkin.
8°	—	46.04
16.7°	45.95	45.93
18.0°	45.90	45.92
42.7°	46.33	45.61
72.4°	46.66	45.25

It will be seen that the numbers given for the temperatures 16.7° and 18° are very nearly the same in both columns, but directly temperatures much above the atmospheric are employed Brühl's numbers rise, whereas mine fall; and this rise is very considerable, being about 0.71 for 55.7°, or about 1.27 for 100°. That the refractive power of a substance should increase in this manner is a result which would not be anticipated.

The two toluidines, ortho- and para-, being stable substances and unlike acetylacetone not changing in structure when heated, are useful for the purpose of comparison. Paratoluidine, however, being solid, and not fusing until about 43° could not, of course, be examined in a pure condition below that temperature, it was, therefore, compared side by side with orthotoluidine at about 49°. The following are the numbers obtained, those given for paratoluidine being the average of three closely concordant sets of determinations made at different periods.

	t.	H _α .	H _β .	H _γ .
Paratoluidine	49.6°	60.642	63.129	64.741
Orthotoluidine	49.0°	60.585	63.028	64.632
<hr/>				<hr/>
Diff.	—	0.057	0.102	0.109

In passing, attention may be drawn to the fact that these differences increase in magnitude with the more refrangible rays, being greatest for H_γ . This indicates a slight difference in the dispersion of the two substances, that of the ortho-compound being the smaller of the two.

Determinations were then made of a solution of paratoluidine in orthotoluidine in molecular proportion, that is, equal weights; also of the orthotoluidine used in making this mixture. The following are the results.

Densities—

Mixture	d 10·4°/4°	1·0005		
Orthotoluidine ..	d 9·7°/4°	1·0074		
	$t.$	$H_{\alpha.}$	$H_{\beta.}$	$H_{\gamma.}$
Mixture	10·4°	1·56745	1·59067	1·60589
Orthotoluidine .	9·7°	1·57110	1·59415	1·60943

Molecular refraction.

	$H_\alpha.$	$H_\beta.$	$H_\gamma.$
Mixture	121·366	126·333	129·588
Orthotoluidine.....	60·658	63·106	64·729
Paratoluidine	60·708	63·227	64·857
Differences between the two toluidines	0·050	0·121	0·128

These differences are very close to those obtained at 49°. It is seen from these results that the ortho-compound gives lower numbers, indicating the same variation in dispersion. The refractive power of the bases is also very similar, but slightly lower at the higher temperature; this has been shown to be invariably the case with all substances yet examined by my apparatus.

Brühl's numbers for paratoluidine at 59·1° give H_α 61·575 and for H_γ 65·459, results which are much higher than mine, and also much higher than he obtained for orthotoluidine at 20°. The latter are practically the same as those obtained in my experiments at 9·7°, thus—

Brühl.	Perkin.
20° 60·70	9·7° 60·658

In the case of the toluidines, therefore, Brühl's results increase as the temperature rises, whilst mine fall very slightly; in fact, wherever Brühl has examined a substance at two widely different temperatures the same fact is observed, thus, in the case of ethylic monocarboxethylacetoacetate, at 21·1°, 81·319 is obtained, but at 70·8, 82·920, and for methylformylcamphor, at 23·1°, 95·191, but at 47·3°, 96·072. These numbers are for $\frac{\mu_x - 1}{d} p$.

As our results agree closely at ordinary temperatures, but differ at higher temperatures, there can be no doubt that the want of accord between our determinations is due to the different instruments we employ. The question then is which is to be taken as giving correct results?

With reference to the apparatus employed in my determinations, one cannot see any reason why a hollow prism, filled with the substance under examination, should not give as good results at 100° as at 15°.

There has not been very much work done by others on the refractive power of compounds at widely different temperatures, the most important being that of Nasini and Bernheimer (*Gazzetta*, 1885, **15**, 59) and (*Jahrsber.*, 1885, 314), who used a hollow prism, heated by passing hot water through the jacket by which it was almost entirely surrounded. With this they obtained results similar to mine, showing that, in the case of stable compounds such as they examined, the molecular refraction does not alter very much with temperature, although it becomes somewhat smaller. The following are examples

	<i>t.</i>	$\frac{\mu_a - 1}{d} p.$	<i>t.</i>	$\frac{\mu_a - 1}{d} p.$
Dimethylnaphthalene	16.4°	93.11	77.7°	92.73
Bromonaphthalene ..	16.5°	90.54	77.6°	90.50
Methylnaphthol	13.9°	88.59	77.7°	88.32
Cinnamic alcohol, ...	24.8°	73.83	77.3°	73.59
Anethoöl	14.9°	82.95	77.3°	82.66

This reduction has been shown to vary with different classes of compounds (*Trans.*, 1892, **61**, 308), and is apparently of the same kind as the temperature differences observed in connection with magnetic rotations.

The agreement in the results obtained with the instrument used by Nasini and Bernheimer and with mine shows that not only the hollow prism, but also that the optical arrangements in both cases, although not identical, acted in the same manner; and, what is more important, the results obtained by Kettler, in his determinations of the refractive power of water, agree closely with mine (*Trans.*, 1892, **61**, 293), although he used an entirely different instrument containing no prism (*Ann. Phys. Chem.*, 1888, **33**, 28). It would seem, therefore, that there must be some unnoticed source of error in the refractometer used by Brühl, when it is employed for temperatures somewhat above those of the atmosphere.

II.—*The Alkaline Reduction of Metanitraniline.*

By RAPHAEL MELDOLA, F.R.S., and ERNEST R. ANDREWS.

THE azoxy- and azo-compounds formed by the alkaline reduction of the nitranilines and their homologues have for some time figured in patent specifications as sources of polyazo-colouring matters, but hitherto little attention has been bestowed on their purely chemical characters. We have for some time past had under investigation the products of the alkaline reduction of metanitraniline, an examination of which was originally undertaken with a view of finding a convenient source of meta-azo-compounds.* Various reducing agents were tried under different conditions, and finally sodium stannite was selected as the most convenient for carrying the reduction to the first stage. We learnt soon after commencing our experiments that Mr. Arthur G. Green had also been working at the subject, and he was good enough to communicate to us the particulars of his method of performing the reduction as well as to place at our disposal specimens of the products which he had obtained. For this information, which has been found of great use, we desire at once to express our thanks to Mr. Green.

Dimetadiamidoazoxybenzene.

In order to prepare this compound, metanitraniline (15 grams) is dissolved in boiling water (1 litre) and a cold solution of sodium stannite (40 grams pure stannous chloride crystals dissolved in 100 c.c. cold water and mixed with 40 grams of solid sodium hydroxide dissolved in 300 c.c. cold water) is slowly added to the boiling solution. On allowing the contents of the flask to cool, the azoxy-compound separates as a yellow substance, crystallising in needles. In order to purify the compound, it is collected, washed with water, dissolved in dilute hydrochloric acid, filtered to remove tarry matter, and the base reprecipitated by ammonia, this operation being repeated till the substance dissolves in acid without leaving any residue. Further purification can be effected by crystallisation from toluene, dilute alcohol, or boiling water. From toluene, the substance separates in large, golden scales, from dilute alcohol in needles, and from water, in which it dissolves only at the boiling temperature, and then

* Concurrently with the above research, I had commenced some experiments on the production of meta-azo-compounds by the action of nitrosobenzene on suitable amido-compounds. The work was interrupted owing to the summer vacation, and Mr. Charles Mills has since entered the same field, and has obtained results similar to mine (Trans., 1895, **67**, 925), so that this part of the investigation is omitted from the present communication.—R. M.

but sparingly, in very slender, yellow needles. The melting point is $146-148^{\circ}$. A very large number of analyses of various preparations have served to convince us that the alkaline reduction of metanitriline is accompanied by the formation of products other than the simple azo- and azoxy-compounds. The azo-compound is, no doubt, simultaneously formed in varying quantities, and its production is unavoidable unless the proportions of sodium stannite and metanitriline mentioned are rigidly adhered to; but, in addition, other compounds containing a higher percentage of carbon are also apparently produced, and become associated with the basic products. We have not been able to isolate any other compound at present, but the great difficulty which we have experienced in obtaining specimens giving correct numbers on analysis has convinced us of the existence of such secondary products. The following results were given by two of the purest preparations.

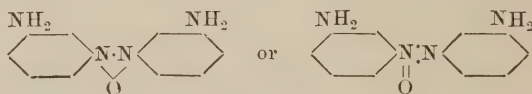
0.1098 gave 0.2554 CO_2 and 0.0534 H_2O . $\text{C} = 63.38$; $\text{H} = 5.37$.

0.1216 „ 24.5 c.c. moist nitrogen at 10° and 765 mm. $\text{N} = 24.26$.

0.1610 „ 34.3 „ „ 15.5° and 755.8 mm. $\text{N} = 24.71$.

$\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}$ requires $\text{C} = 63.15$; $\text{H} = 5.26$; $\text{N} = 24.56$ per cent.

The constitution of the compound is expressed by one of the two formulæ—



It is a strong base dissolving readily in all mineral acids and in the stronger organic acids; most characteristic is the insolubility of the dihydrochloride, $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O} \cdot 2\text{HCl}$, in excess of hydrochloric acid, the salt being at once precipitated in the form of a whitish, crystalline powder on adding strong acid to the solution of the base in dilute acid. The base dissolves more or less readily in all the usual organic solvents, its solutions being orange; it is not volatile in steam to a sufficient extent to enable it to be purified by this means. Of its derivatives, Mixer has prepared the dibenzoyl compound by reducing benzoylmetanitrilide with zinc and alcoholic ammonia (*Amer. Chem. J.*, 1883, **5**, 5), and gives the melting point as about 272° . We have prepared the diacetyl derivative by boiling the base for about half an hour with acetic anhydride in acetic acid solution, and crystallising the product from boiling glacial acetic acid, in which it dissolves but sparingly. It forms an ochreous powder consisting of micro-crystalline nodules melting at 254° .

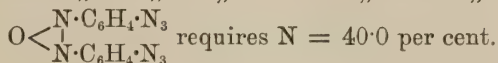
0.1161 gave 0.2626 CO_2 and 0.0566 H_2O . $\text{C} = 61.67$; $\text{H} = 5.34$.

0.2638 „ 39.3 c.c. moist nitrogen at 11° and 766.7 mm. $\text{N} = 17.89$.

$\text{O} < \begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O} \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O} \end{array}$ requires $\text{C} = 61.53$; $\text{H} = 5.12$; $\text{N} = 17.94$ p. c.

The bisazimide was also prepared by diazotising in hydrochloric acid solution, precipitating the diazoperbromide and treating the latter with ammonia (Meldola and Hawkins, Proc., **8**, 133). After crystallisation from petroleum, it was obtained in the form of nodular, ochreous crystals, which become darker on exposure to light.

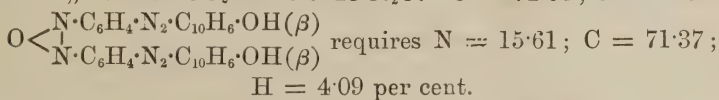
0.1792 gave 62.1 c.c. moist nitrogen at 15.5° and 753.5 mm. $N = 40.09$.
 0.0888 „ 29.9 „ „ „ 13° „ 763.1 „ $N = 39.88$.



This compound melts at $85-86^{\circ}$, and explodes when heated in a dry tube above its melting point. The yield is not good, as the bisazimide is contaminated with a considerable quantity of a resinous compound, from which it must be separated by extraction with hot, dilute alcohol, preferably with the addition of animal charcoal, before it is in a condition for crystallisation from petroleum.

The diamidoazoxy-compound is very readily diazotised by the usual methods, and the tetrazo-salts enter at once into combination with amines and phenols to form colouring matters. As a typical azo-compound, that produced by combination with β -naphthol was prepared for analysis. The tetrazo-chloride is prepared in the usual way, and the solution mixed with the necessary quantity of β -naphthol, freshly precipitated by acid from its solution in alkali and suspended as a pulp in the liquid; no colour appears at first, but on gradually making the mixture alkaline with ammonia, a red tint develops, and, after some hours, a brilliant red precipitate of the azo-colouring matter is formed. The substance, after being collected, washed, and dried, was purified by repeated crystallisation from boiling aniline; it then formed small, dull, red needles melting at $244-245^{\circ}$.

0.1167 gave 15.3 c.c. moist nitrogen at 11.4° and 764.2 mm. $N = 15.67$.
 0.1104 „ 14.5 „ „ „ 12.75° „ 766.1 „ $N = 15.64$.
 0.1015 „ 0.2665 CO_2 and 0.0423 H_2O . $C = 71.61$; $H = 4.63$.



The azo-compound dissolves in strong sulphuric acid with a magenta-red colour, and is precipitated unchanged on dilution with water.

In order to connect the diamidoazoxybenzene with a known compound of the same type prepared by another method, a specimen was diazotised, and the amido-groups replaced by iodine by treating the tetrazo-sulphate with potassium iodide. Much resin was formed,

but the product, when extracted with alcohol, furnished a crystalline compound consisting of ochreous needles melting at 118—119°, and having the composition of diiodoazoxybenzene.

0.1170 gave 6.7 c.c. moist nitrogen at 16° and 753.4 mm. $N = 6.61$.
 0.1426 „ 0.1476 AgI. $I = 55.92$.

$O < \begin{array}{c} N \cdot C_6H_4I \\ | \\ N \cdot C_6H_4I \end{array}$ requires $N = 6.24$; $I = 56.35$ per cent.

This compound is probably identical with that obtained by Gabriel by reducing metaiodonitrobenzene with alcoholic potassium hydroxide (*Ber.*, 1876, **9**, 1408).

Dimetadiamidoazobenzene.

After many experiments with an increased quantity of sodium stannite under various conditions, we finally abandoned this reducing agent as a means of passing from the azoxy- to the azo-compound. It has been found more advantageous to use for this purpose zinc dust and sodium hydroxide in the following way.

The azoxy-compound is dissolved in a small quantity of alcohol, and an equal weight of sodium hydroxide dissolved in a little water is added to the alcoholic solution contained in a flask. A quantity of zinc dust, about twice the weight of the azoxy-compound, is then added, and the contents of the flask kept warm on a water bath for some hours, with frequent agitation; the solution gradually becomes decolorised, owing to the formation of a hydrazo-compound; when this stage is reached, the solution is at once filtered to remove the excess of zinc, and on exposure to the air for a few hours the hydrazo-compound is completely oxidised and the azo-compound regenerated, as indicated by the orange colour of the solution. By this means only can the complete reduction of the azoxy-compound be insured. Potassium hydroxide cannot be conveniently used, as this carries the reduction too far, the yield of azo-compound being small and meta-phenylenediamine being formed.

The purification of the azo-compound is best effected by crystallisation from water; for crystallisation from organic solvents, especially hydrocarbons, has a tendency to render the compound impure, as it appears to be capable of entering into combination with and obstinately retaining some of the solvent. The alcoholic solution containing the azo-compound, prepared in the manner described, is transferred to a flask, diluted with water, and all the alcohol distilled off; the orange-coloured, crystalline residue is collected, washed with cold water, and dissolved in a large volume of water by means of a little hydrochloric acid. The solution of the hydrochloride is then raised to the boiling point, made alkaline with ammonia, and filtered

rapidly while still hot; on cooling, the azo-compound separates in dull, orange-coloured needles. This method of purification is more effective than the direct solution of the azo-compound in boiling water, as the crystals when once formed dissolve with great difficulty; the treatment can be repeated till the hot solution passes through the filter without leaving any residue. The readiness with which the azo-compound combines with other substances renders it a matter of considerable difficulty to prepare specimens sufficiently pure for analysis. Until the above method of preparation and purification was adopted, our products all gave a percentage of nitrogen below that required by the formula of the azo-compound, and for some time we were under the impression that the treatment of the azoxy-compound with zinc dust and alkali had not removed oxygen, but had effected transformation into an isomeride, possibly stereochemical. The melting point (after drying at 110—120°) is 150—151° when pure.

0.0962 gave 21.45 c.c. moist nitrogen at 14.2° and 762.7 mm. N = 26.27.
 0.0479 „ 10.9 „ „ 20° „ 768.3 „ N = 26.27.

$\begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \\ || \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \end{array}$ requires N = 26.41 per cent.

In order to characterise this compound further, the bisazimide was prepared by the usual method, but the yield is extremely small, and the melting point the same as that of the bisazimide obtained from the azoxy-compound (86°), so the product was not further examined.

The diacetyl derivative was prepared by dissolving the base in glacial acetic acid mixed with acetic anhydride, and heating at 100° for an hour. The product was purified by crystallisation from glacial acetic acid, in which it dissolves somewhat more readily than the corresponding diacetylazoxy-compound, but as the analytical results still indicated that an impurity was present, it was finally obtained pure by crystallisation from boiling aniline.

0.0852 gave 14.15 c.c. moist nitrogen at 20° and 759.5 mm. N = 18.96.
 0.0865 „ 14.5 „ „ 21° „ 759.4 „ N = 19.05.
 0.1992 „ 0.4753 CO₂ and 0.0959 H₂O. C = 65.08. H = 5.34.

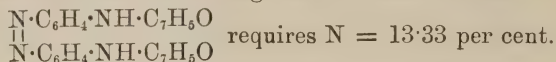
$\begin{array}{c} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O} \\ || \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_2\text{H}_3\text{O} \end{array}$ requires N = 18.92; C = 64.86; H = 5.40 p. c.

This acetyl derivative is very similar in appearance and properties to that obtained from the diamidoazoxy-compound; it forms a micro-crystalline powder (small needles from aniline) of a somewhat more orange colour than the latter acetyl derivative. It begins to shrink at 268°, and melts completely at 272°.

The dibenzoyl derivative was prepared by suspending the crystal-

line base in warm water, adding the calculated quantity of benzoyl chloride, and then agitating briskly with the gradual addition of sodium hydroxide till the solution had become slightly alkaline. The product was collected, washed, and dried, and then crystallised from boiling aniline. It forms straw-coloured, microscopic needles, melting at 284—285°.

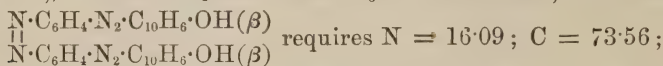
0.1387 gave 16.35 c.c. moist nitrogen at 20.5° and 756 mm. N = 13.36.



The diamidoazo-compound is converted by nitrous acid, in the presence of hydrochloric acid, into a tetrazo-chloride, with the same facility that the diamidoazoxy-compound undergoes this transformation. Combination with β -naphthol was effected in the same manner as with the previous compound. The trisazo-compound, after crystallisation from aniline, consists of small, red needles, duller in shade than the corresponding bisazo-azoxy-compound.

0.1405 gave 19 c.c. moist nitrogen at 10.3° and 755.3 mm. N = 16.05.

0.0881 „ 0.2380 CO₂ and 0.0395 H₂O. C = 73.68; H = 4.98.



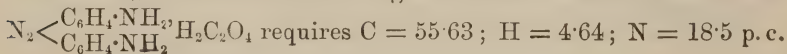
H = 4.21 per cent.

The substance melts at 282°, and dissolves in strong sulphuric acid with a magenta colour, which is perceptibly bluer than the colour given by the corresponding azoxy-compound, the difference between the two becoming more pronounced on diluting with a little water. Like all the azo-derivatives of β -naphthol, it is destitute of phenolic characters, being quite insoluble in boiling aqueous alkali. It dissolves in boiling alcoholic potash with a red coloration, which is indistinguishable from that given by the azoxy-compound under the same conditions.

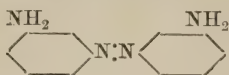
Of the salts of dimetadiamidoazobenzene, the oxalate is very characteristic. It is formed by adding a solution of oxalic acid to a boiling aqueous solution of the base; the salt separates at once in the form of ochreous scales, which are but slightly soluble, even in hot water. The dry salt has no definite melting point, but chars at 205—210°. A specimen dried at ordinary temperatures over strong sulphuric acid in a desiccator for some days was analysed with the following results.

0.1502 gave 0.2050 CO₂ and 0.0626 H₂O. C = 55.38; H = 4.63.

0.1064 „ 16.5 c.c. moist nitrogen at 15° and 765 mm. N = 18.29.



From its mode of formation, the diamidoazo-compound may be represented as having the constitution



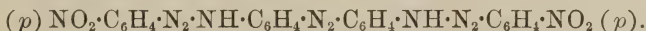
This was confirmed by displacing the NH_2 -groups by iodine by means of the diazo-reaction. The diiodoazobenzene crystallises in orange scales melting at $150\text{--}151^\circ$ (Gabriel, *Ber.*, 1876, **9**, 1410), and is identical with the compound produced by the alkaline reduction of metanitroiodobenzene.

0.0718 gave 4 c.c. moist nitrogen at 10.5° and 758.3 mm. $\text{N} = 6.61$.

$\text{C}_6\text{H}_4\text{I} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4\text{I}$ requires $\text{N} = 6.45$ per cent.

As the para-position with respect to the azo-group is open in both benzene rings in the above formula, it appeared of interest to try whether one molecule of the compound would combine with two molecules of a diazo-salt, so as to form a tertiary azo-compound of the type $\text{X} \cdot \text{N} \text{ : } \text{N} > \text{C}_6\text{H}_4 \cdot \text{N} \text{ : } \text{N} \cdot \text{C}_6\text{H}_4 < \text{N} \text{ : } \text{N} \cdot \text{X}$.

It was found, however, that the base did not combine with diazobenzene chloride, so a more acid diazo-salt, namely, paranitrodiazobenzene chloride was used; combination took place with this diazo-salt in the presence of sodium acetate, and a brown, amorphous substance separated. The latter has all the properties of a diazoamide and not of an azo-compound; it dissolves readily in alcoholic sodium hydroxide in the cold with a magenta colour, and with a similar colour in hot aqueous, caustic soda solution; it is reprecipitated from its alkaline solutions as a flocculent, ochreous substance on the addition of acids. The compound is uncrystallisable, and could not therefore be obtained pure; it melts with decomposition at about $198\text{--}200^\circ$. A determination of nitrogen gave results agreeing fairly well with the formula of the bisdiazoamide.



We have no doubt that this is the compound formed under the conditions described.

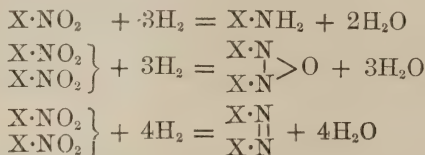
Remarks on the Reduction of Nitro-compounds.

By R. MELDOLA.

The extreme readiness with which meta- and para-nitraniline* give azoxy- and azo-compounds under the influence of alkaline reducing

* Orthonitraniline does not give an azoxy-compound when reduced with sodium stannite under the same conditions as metanitraniline; it is partly reduced to orthophenylenediamine and partly left unchanged.

agents, whilst passing with equal readiness into the respective diamines under the influence of acid reducing agents, has always appeared to me one of the most striking examples of the difference in behaviour of nitro-compounds, according to the mode of reduction, that is, acid or alkaline. In dealing with the theory of the reduction of nitro-compounds the equations



can obviously be considered only as expressing the final results of a series of intermediate transformations. Of the nature of these intermediate stages, nothing was known definitely till E. Hoffmann and Victor Meyer showed that nitro-compounds of the paraffin series gave hydroxylamine derivatives on reduction with stannous chloride (*Ber.*, 1891, **24**, 3528; methylhydroxylamine from nitromethane).

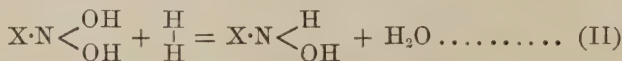
The remarkable discovery by Bamberger (*Ber.*, 1894, **27**, 1347 and 1548), and Wohl (*ibid.*, 1432) that nitrobenzene can be reduced to β -phenylhydroxylamine by zinc dust and water, may be taken as another proof that the mechanism of the process of reduction is not simply represented by the withdrawal of oxygen from the nitro-group.

The remarks which I now venture to offer are to be regarded in the light of a tentative contribution to the theoretical side of this question. Much more experimental evidence will be required before a complete theory of the process can be formed, but it appears desirable to call attention at once to the necessity of remodelling the existing crude notions respecting a transformation of such general scientific and technical importance. The following attempt to indicate, at least, a possible series of steps may be found sufficiently suggestive to prompt further investigation, even if destined to be displaced by other hypotheses as our knowledge grows.

Under all conditions, the first action of the reducing agent may be regarded as being the hydroxylation of the nitro-group.

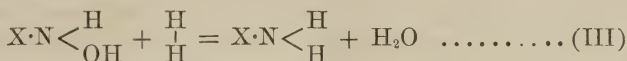


The derivative of the hypothetical dihydroxylamine being too unstable to exist, is reduced by further action, thus—

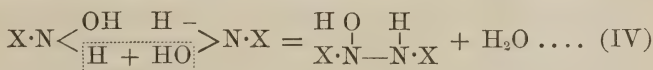


At low temperatures, and with weak reducing agents, the hydroxyl-

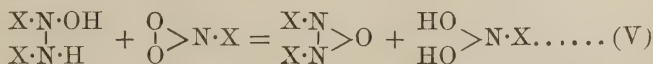
amine stage can be retained as a resting stage in certain cases. At high temperatures, and with strong reducing agents, the second hydroxyl group is replaced.



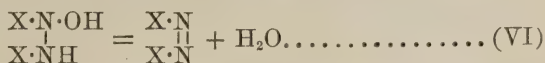
This view would represent the ordinary conversion of a nitro-compound into an amine by the usual methods; it assumes that the hydroxylamine stage is passed through rapidly and imperceptibly, unless special means are taken for arresting the process at that stage. Under other conditions, of which the presence of alkali appears to be the most favourable, and, in a less degree, the access of atmospheric oxygen (Bamberger, *loc. cit.*, 1550), the hydroxylamine derivative undergoes "condensation" with the formation of an azoxy- or an azo-compound. To bring about this result two molecules must coalesce, and from general considerations concerning such processes of condensation it seems feasible to represent the change, thus—



The intermediate compound at this stage would be a derivative of the (at present) hypothetical hydroxy-hydrazine, $\text{H}_2\text{N}\cdot\text{NH}\cdot\text{OH}$. The assumption that such a compound is formed harmonises well with the facts, because both the azoxy- and the azo-type are derivable therefrom, the former by oxidation and the latter by a repetition of the "condensing" process. These two possibilities are best considered separately. In the first place, the oxidation of such a compound would give rise to an azoxy-compound; unattacked nitro-compound would act as oxidising agent, or, when all the nitro-compound is reduced to Stage I (see equation), atmospheric oxygen might be effective, as found by Bamberger.

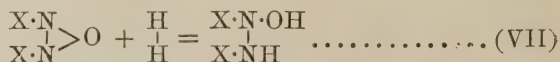


In the next place, the further (inner) condensation of the hydroxy-hydrazine derivative would give rise to an azo-compound which, from this point of view, is the inner anhydride of its generator—



The hypothesis thus suggests that azoxy-compounds arise, not by *direct* reduction of nitro-compounds, but by the oxidation of intermediate hydroxy-hydrazines—as long as unaltered nitro-compound is present the azoxy-compound can be continuously formed. No azo-compound could be formed at this stage because the oxidising action

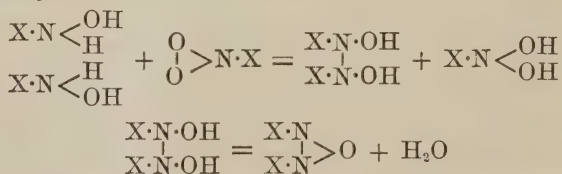
on the hydroxy-hydrazine is greater than the tendency to condense to the azo-stage (Equation V). But, when all the nitro-compound is used up, the formation of azoxy-compound has reached its maximum, and the reducing agent can act directly, while condensation to the azo-stage can also take place. The question thus arises as to the action of the reducing agent when the azoxy-stage has reached its maximum. It seems to me that the direct removal of oxygen is again an improbable explanation. The most likely product is the intermediate hydroxy-hydrazine.



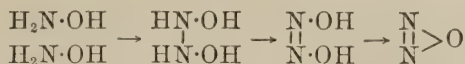
As no oxidising agent is present at this stage, the azo-condensation (Equation VI) can now go on continuously.

These suggestions are well worthy, as I venture to think, of being submitted to the crucial test of experiment; certainly they are in harmony with the well-known fact that the azo-compounds are only obtained by alkaline reduction, as the last stage (unless the reduction be carried on to the hydrazo-stage) of a protracted operation. It appears desirable to reinvestigate in the light of the present hypothesis the products of the reduction of azoxy-compounds, and also to ascertain whether the exclusion of air during the process of alkaline reduction would accelerate the production of azo-compounds. These and other collateral points suggested in the course of this theoretical discussion will be dealt with experimentally in the course of the present session.

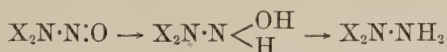
An alternative series of stages from the hydroxylamine derivative (Equation II) may also be suggested. The oxidising action of unaltered nitro-compound might be regarded as taking place in the following way.



The azoxy-compounds on this view also are anhydrides of intermediate compounds, namely, derivatives of dihydroxy-hydrazine. The action of mild oxidising agents (atmospheric oxygen) does convert phenylhydroxylamine into azoxybenzene, whilst strong oxidisers convert it into nitrosobenzene (Bamberger and Wohl). In harmony, likewise, with this view is the fact that hydroxylamine itself, under the influence of oxidising agents, evolves nitrous oxide, a decomposition which may be brought into line with the above hypothesis.



The prototype of the azoxy-compounds is thus nitrous oxide or its dihydro-derivative, which is at present unknown. From this point of view the generally accepted formula of the azoxy-compounds is preferable to the formula $\text{X}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{N}}}\cdot\text{N}\cdot\text{X}$, corresponding to Strecker's formula for the diazoamides. Another point in favour of some such view of the course of reduction of nitro-compounds, as is here advocated, is that it gives prominence to the analogy with the process of reduction of nitroso- and isonitroso-compounds.



It is unnecessary to elaborate these suggestions from the speculative side in greater detail at present, but it will appear from the foregoing that such an apparently simple change as the conversion of a nitro-compound into an amine is by no means so well understood as the crude equations generally given would lead us to suppose.

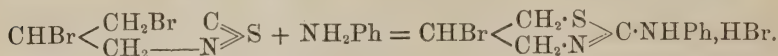
III.—*The Chemistry of Dibromopropylthiocarbimide; and the Action of Bromine and of Iodine upon Allylthiourea.*

By AUGUSTUS E. DIXON, M.D.

IN a short communication, made a few years ago to this Society (Trans., 1892, **61**, 545), I showed that bromine unites readily with allylthiocarbimide, thereby producing $\beta\gamma$ -dibromopropylthiocarbimide, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{NCS}$, a dense, almost colourless oil, of high refractive power, volatile in a current of steam, nearly insoluble in water, miscible with alcohol, possessing the characteristic odour, and, generally speaking, the ordinary properties of a liquid thiocarbimide.

In its chemical relations, however, it manifested certain peculiarities; thus, for example, it combined readily, on warming, with aniline, but instead of affording the expected dibromopropylphenylthiocarbamide, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, 1 mol. HBr was eliminated, the product being the hydrobromide of a closed-chain basic compound, from which the free base, a solid, was liberated by

treatment with caustic alkali. For reasons set forth in the paper mentioned, the action was believed to occur, ultimately, as follows.



Further, the thiocarbimide interacted spontaneously with alcoholic ammonia, but instead of dibromopropylthiourea, ammonium bromide was obtained, together with a viscid, basic syrup, which refused to crystallise, and was not then further examined.

That the constituents in question should fail to afford dibromopropylthiourea, was, at the time, a matter of surprise, especially as the latter compound appeared, on reference to Beilstein's *Handbuch*,* to have been already prepared and examined by Maly, who obtained (*Zeit. f. Chem.*, 1867, 42), from bromine and allylthiourea, a well-defined solid substance, $\text{C}_4\text{H}_8\text{N}_2\text{SBr} = ? \text{CSN}_2\text{H}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$.

Returning later, however, to the study of this and similar compounds, their properties seemed hardly to accord with the above constitution; thus, according to Maly, the dibromide, $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{Br}_2$, when treated with moist silver chloride, exchanged but 1 atom of bromine for chlorine, producing the chlorobromide, $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{BrCl}$; again, with moist silver oxide, a strongly alkaline hydroxybromide,



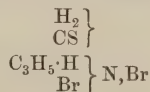
was formed, from which, by the action of hydrochloric acid, the chlorobromide was regenerated.

Maly did not fail to notice the significance of these peculiarities, for he refers expressly to the special function of one bromine atom, which acts like the bromine in ammonium bromide;† in the case of the chlorobromide, the chlorine atom plays an analogous part

Moreover, further experiments on the interaction of ammonia with dibromopropylthiocarbimide suggested the desirability of re-examining the dibromo-derivative; and this has now been done, with results leading to the conclusion that it and the other allied substances (including a di-iodide) are not halogenised thioureas, but salts of basic ring-compounds, derived probably from the parent-

* Unfortunately I had not then access to the original paper.

† "Giebt man dem Thiosinnaminbromür folgende Formel:



in der ein Atom Brom das eine Ammoniak zum Ammonium macht, also innerhalb des Radicals steht, während das zweite die Stelle einnimmt, wie das Brom im Bromammonium, oder das Chlor im Salmiak, so ist wohl zu erwarten, dass sich diese beiden Bromatome verschieden verhalten werden" (*loc. cit.*).

type, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{NH}_2$, that is, μ -amidopenthiazoline, or, using the nomenclature proposed by me (Trans., 1895, **67**, 564), trimethylene- ψn -thiourea.

BROMINE AND ALLYLTHIOUREA.

The addition product, $\text{C}_4\text{H}_8\text{N}_2\text{S} \cdot \text{Br}_2$, was prepared by adding 1 mol. of bromine, dissolved in chloroform, to allylthiourea (1 mol.) in alcohol; cooling by means of a freezing mixture had little influence on the yield, which amounted, in one case, where it was employed, to $72\frac{1}{2}$ per cent. of the theoretical, and in another, where it was not, to 71 per cent. After removing all the solid matter, a residue was obtained, consisting of a rather dark brown syrup, which, at the temperature of the water bath, evolved fumes of hydrogen bromide. The solid product deposited slowly; it was, as described by Maly, soluble in water and alcohol, very easily in the former, more sparingly in the latter; in other solvents, it was insoluble, or nearly so. Its melting point fell somewhat below that given, namely 146 — 147° ; I observed in two successive preparations 139 — 140° and $139\cdot5$ — $140\cdot5^\circ$ (corr.), respectively, apparently without decomposition.

The aqueous solution had an acid reaction, was not desulphurised by treatment with alkaline lead tartrate, and yielded with ammoniacal nitrate of silver a whitish precipitate (not readily affected by exposure to sunlight), which did not blacken even on boiling the mixture. Presumably, therefore, the compound was not a monosubstituted thiourea (Dixon, Trans., 1893, **63**, 319).

Action of Caustic Alkali.—On the addition of strong caustic potash (or even ammonia) to the aqueous solution, a heavy basic oil was precipitated, containing nitrogen, sulphur, and bromine. The supernatant clear liquid, when acidified and treated with chlorine water, reacted freely for bromine; moreover, with silver nitrate, it gave a yellowish precipitate of silver bromide. Thus a partition of the bromine had occurred, a probable explanation of which, in view of the above phenomena, lay in the abstraction by the alkali, from the original substance, of a mol. of hydrogen bromide—



and the results of a roughly quantitative experiment went to support this idea; 5.1 grams of the dibrominated compound yielding nearly 3.5 grams of basic oil, whilst, according to the equation, 3.6 grams should have been obtained.

The oil is clear, almost colourless, miscible with spirit, soluble in

much cold water, or moderately at the boiling temperature; it is strongly alkaline to litmus, has a barely perceptible basic odour, and when dissolved in dilute hydrochloric acid, reacts freely with chlorine water for bromine. If exposed for some time to air, it darkens, becomes hard, and insoluble in spirit; it dissolves now only slowly in boiling hydrochloric acid, from which it is precipitated by alkali as an amorphous, whitish powder; the latter, on heating, swells up and carbonises without melting; it appears also to be insoluble, save in liquids which decompose it. The nature of these latter changes was not investigated.

Action of Hydrobromic acid.—Dilute hydrobromic acid was added in slight excess, to a quantity of the freshly precipitated base; the mixture was at first turbid, but became clear as the point of neutralisation was approached; the solution was then evaporated to a small bulk on the water bath, and left overnight; white crystals separated, freely soluble in water, having the appearance, and exhibiting all the properties, of the compound obtained by the direct union of bromine with allylthiourea, and melting, after recrystallisation, at the same temperature, namely, $139-140^{\circ}$.

Action of Hydrochloric acid.—If, then, Maly's allylthiourea dibromide is the hydrobromide of a base, $C_4H_7N_2SBr$, the latter, on treatment with hydrochloric acid, ought to afford a hydrochloride, $C_4H_7N_2SBr, HCl$, identical with the chlorobromide obtained by him from the dibromide and moist silver chloride. This is, in fact, the case, as shown by the following experiment.

A quantity of the basic oil was treated with a slight excess of hydrochloric acid, and the clear solution concentrated by evaporation on the water bath; on cooling, beautiful rosettes of long, very hard, white prisms were deposited, having the properties ascribed to the chlorobromide, and melting, after being previously well washed with spirit, at the temperature recorded by Maly, namely $129-130^{\circ}$. This compound, like the hydrobromide itself, reacts freely for bromine on the addition of chlorine water. From this synthesis, it may be concluded that the single bromine atom which the "dibromide" gives up on treatment with moist silver chloride is the one not included in the $C_4H_7N_2SBr$ fraction of the molecule.

It seemed of interest to try whether dibromopropylthiocarbimide would exchange any of its bromine for chlorine under the above treatment; an experiment was therefore made by allowing the thiocarbimide, in aqueous spirit, to remain (in the dark) in contact with excess of freshly precipitated silver chloride, shaking frequently. After 10 days, during which interval slight desulphurisation had occurred, the mixture was heated for a few minutes, and then steam distilled; a brilliant oil came over, in which the sulphur and nitrogen

were determined, with the result that it proved to be the unchanged dibromopropylthiocarbimide.

Action of Picric acid.—In order to obtain the base in a form which admitted of easy purification for analysis, it was converted into the picrate, either by treating the liquid base in alcoholic solution with picric acid, or by adding the latter to an aqueous solution of the hydrobromide, got from bromine and allylthiourea. In either case, a finely divided, canary-yellow precipitate fell, which, on recrystallisation from dilute spirit, was obtained in minute, glittering, pale-yellow prisms, melting at $187-188^{\circ}$ (corr.). If heated rapidly over a gas flame, it melts, begins to effervesce, and then deflagrates, leaving a porous, carbonised residue.

The picrate is rather sparingly soluble in boiling water, still less so in cold; more easily, though by no means freely, in boiling alcohol. It is oxidised by boiling with nitro-hydrochloric acid, with formation of sulphuric acid, but yields no sulphur to boiling alkaline, lead, or silver solutions.

The formula was checked by analysis.

0.2017 gave 0.2074 CO_2 , and 0.0565 H_2O . $\text{C} = 28.04$; $\text{H} = 3.11$.

0.2074 „ 29.4 c.c. moist nitrogen at 15° and 759 mm. $\text{N} = 16.59$.

0.2992 „ 0.1683 BaSO_4 . $\text{S} = 7.73$.

$\text{C}_4\text{H}_7\text{N}_2\text{SBr}, \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ requires $\text{C} = 28.28$; $\text{H} = 2.36$;
 $\text{N} = 16.55$; $\text{S} = 7.55$ per cent.

These figures—although that for the hydrogen is unduly high—suffice to establish the composition of the base as $\text{C}_4\text{H}_7\text{N}_2\text{SBr}$, and not $\text{C}_4\text{H}_8\text{N}_2\text{SBr}(\text{OH})$; the latter, Maly's *bromthiosin ammoniumoxyhydrat*, would require $\text{C} = 27.13$; $\text{H} = 2.26$; $\text{N} = 15.88$; $\text{S} = 7.25$. The percentage composition of this compound differs only slightly from that of the base $\text{C}_4\text{H}_7\text{N}_2\text{SBr}$ (even assuming them both to be uncombined), and it seems not unlikely that the material analysed* by him was the base in question, possibly containing moisture, or else slightly impure.

Ammonia and Dibromopropylthiocarbimide.

The chemistry of the interaction between allylthiourea and bromine having been thus far cleared up, an investigation of that between ammonia and dibromopropylthiocarbimide was now proceeded with. Previous experiment had, as already stated, established the non-formation from these constituents of dibromopropylthiourea; but the facts which had meanwhile come to light pointed to such a negative result as at least probable, for the union of the compounds in question might be expected to result in the production of the hydro-

* No analysis is given in his paper.

bromide of the brominated base, and since this salt is decomposed by ammonia, as shown above, the products to be anticipated are those which were actually obtained, namely, a basic oil, together with ammonium bromide,



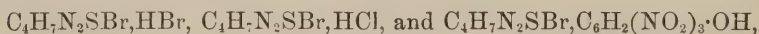
Dibromopropylthiocarbimide was dissolved in a considerable excess of strong alcoholic ammonia; interaction commenced in a few seconds, with evolution of so much heat that the mixture began to boil, and, on cooling, crystals of ammonium bromide were deposited. When evaporated as far as possible on the water-bath, the product consisted of a brownish oil, mixed with solid matter; this was treated with excess of dilute hydrobromic acid, again evaporated, and extracted with absolute alcohol, which left most of the ammonium bromide undissolved, and by repeating the evaporation and extraction, a little more ammonium bromide was removed. The clear solution was then mixed with a few drops more of dilute hydrobromic acid, and allowed to evaporate spontaneously; next day a crop of solid matter had formed, entangled in a tenacious mother liquor; the latter was drained off, not without difficulty, by aid of the pump, and the residue recrystallised from water, and well washed with spirit. The product was colourless, freely soluble in water, soluble in alcohol, had an acid reaction, gave, on the addition of caustic potash, a basic oil, afforded bromine when treated with chlorine water, and in short, resembled precisely the hydrobromide obtained from allylthiourea; its melting point was $139\text{--}140^\circ$ (corr.), that is, identical with that observed for the said hydrobromide.

For further identification, the thiocarbimide and ammonia were combined as before, the precipitated ammonium bromide was dissolved by adding water, and the oil by dilute hydrochloric acid; the clear solution, when mixed with caustic alkali, deposited a basic oil, which was dissolved in spirit and a little hydrochloric acid, and treated with picric acid. It gave a somewhat viscid, yellow precipitate, which, after recrystallisation, had the appearance and general properties of the picrate already described, melting at nearly the same temperature, namely, $183\text{--}184^\circ$ (corr.).

Summarising the principal facts elicited from the above experiments, it may be stated that—

1. Bromine unites directly with allylthiourea to form a compound, $\text{C}_4\text{H}_8\text{N}_2\text{SBr}_2$; this compound is the hydrobromide of a strong base, $\text{C}_4\text{H}_7\text{N}_2\text{SBr}$, which is liberated from it as an oil on the addition of caustic alkali.

2. The free base combines with hydrobromic, hydrochloric, and picric acids, yielding



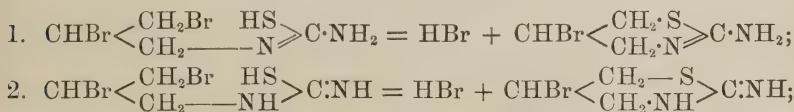
respectively. The first of these is identical with the addition product of allylthiourea and bromine.

3. The same base, together with ammonium bromide, is formed by the action of alcoholic ammonia on dibromopropylthiocarbimide.

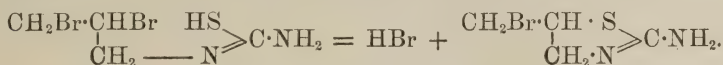
Constitution of the Base, C₄H₇N₂SBr.—The mechanism by which the above base is produced may be explained as follows.

First, having regard to the very favourable conditions realised for its formation, the initial stage consists, probably, in the production of (an unstable) dibromopropylthiourea; and since the mono-substituted thioureas, at all events when undergoing chemical change, and particularly under the influence of substances containing halogen, assume generally the "labile" form, the base may be supposed to originate from the decomposition of either C₃H₅Br₂·N:C(SH)·NH₂, or C₃H₅Br₂·NH·C(SH):NH.

Secondly, the tenacity with which the base retains its sulphur, not only on treatment with alkaline lead solution, but even after boiling with the much more potent ammoniacal silver nitrate, points strongly to the existence of a sulphur atom, held in closed chain between two other polyvalent atoms. Such a linkage would necessarily entail the withdrawal of the SH hydrogen (to form hydrogen bromide), and the action would then occur in one of the two following ways, probably the former.



with, of course, the alternative possibility that the bromine in the β -position might be removed instead, for example,



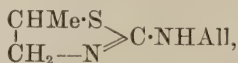
Moreover, these structures accord much better with the highly basic character of the substance than those where the SH is supposed to persist, for instance, CHBr < $\begin{array}{c} \text{CH}_2 \text{---} \text{N} \\ \text{CH}_2 \cdot \text{NH} \end{array}$ > C·SH.

Other evidence of a more direct kind goes to confirm the views above stated. By combining methylthiocarbimide with bromethylamine, Gabriel obtained (*Ber.*, 1889, **22**, 1148), not methyl-bromethylthiocarbimide, CH₃·NH·CS·NH·CH₂·CH₂Br, but the hydrobromide of a base, "*n*-methyl-ethylene- ψ -thiourea,"

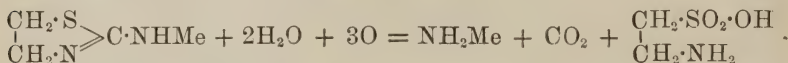


* In the same paper, he conjectures (p. 1145) that Maly's dibromide,

Hirsch, in like manner, starting from β -bromopropylamine, prepared (*Ber.*, 1890, **23**, 971) with methyl and allylthiocarbimides, the "propylene" derivatives, $\begin{smallmatrix} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2\text{---N} \end{smallmatrix} \gg \text{C}\cdot\text{NHMe}$, and

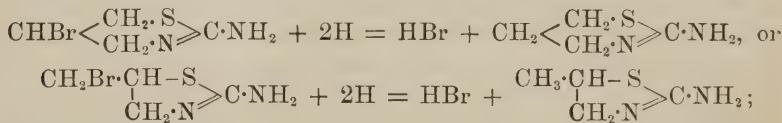


respectively; the structure of these compounds was established by their behaviour on oxidation, the first-named, for example, yielding methylamine, carbonic anhydride, and taurine.



These and other similar experiments by Gabriel and his pupils, have shown the easy mobility of a halogen atom, under the circumstances mentioned; whence, by analogy, the general structure of the basic dibromopropylthiocarbimide derivative may be inferred, save as regards the position of its bromine. It has been pointed out, however, by Paal (*Ber.*, 1891, **24**, 4253) that bromine is more readily eliminated from the γ than from the β -position (see also Andreasch, *Monatsh.*, 1889, **5**, 33); the constitution of the base is, therefore, presumably $\text{CHBr} < \begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ | \\ \text{CH}_2\cdot\text{N} \end{smallmatrix} \gg \text{C}\cdot\text{NH}_2$,* that is, μ -amido- γ -bromopenthi-azoline. Regarded as a dihydric thiourea derivative, and marking the points of substitution in the carbon ring, α , β , γ , reckoning from the nitrogen attachment (n) of the latter, its structure may also be systematically expressed, according to the nomenclature referred to above, by the name β -bromotrimethylene- ψn -thiourea.

It was hoped that by reduction of the base with nascent hydrogen, its bromine might undergo replacement, and the position of the latter be directly ascertained by the production of either trimethylene- or propylene-pseudothiourea, thus



but the methods tried, namely, treatment with sodium amalgam, or with tin and hydrochloric acid, led only to disruption of the molecule.

$\text{C}_4\text{H}_8\text{N}_2\text{SBr}_2$, should be regarded as the hydrobromide of a similarly constituted base; I only noticed this statement after practically all the work in this paper had been completed.

* Probably capable of interacting also, under suitable conditions, in the desmotropic form, $\text{CHBr} < \begin{smallmatrix} \text{CH}_2\text{---S} \\ | \\ \text{CH}_2\cdot\text{NH} \end{smallmatrix} \gg \text{C}\cdot\text{NH}$.

The readiness with which the brominated thiocarbimide parts with an atom of its halogen, thereby forming the haloïd salt of a base (or free hydrogen bromide) will be seen from what follows, to be as marked with primary and secondary amines (and even with alcohols) as in the case of ammonia; it seems, in fact, as though the brominated thioureas,* mono-, di-, or tri-substituted, are all alike incapable of existence under ordinary conditions. The question arises, therefore, whether, having regard to the apparent similarity of the cases to those above-mentioned, the "chlorallylthiourea" and "bromallylthiourea," briefly recorded by Henry (*Ber.*, 1872, 5, 188), as resulting from the action of ammonia on α -chlor- and brom-allylthiocarbimides, respectively, are not also haloïd salts, namely, the hydrochloride and hydrobromide of a basic ring compound,

$$\begin{array}{c} \text{CH}_2\text{:C} \text{---} \text{S} \\ \text{CH}_2\text{:N} \text{>} \text{C} \cdot \text{NH}_2. \end{array}$$

I hope, later on, to re-examine these substances.

IODINE AND ALLYLTHIOUREA.

By combining the above materials in alcoholic solution, Maly obtained (*Zeit. f. Chem.*, 1869, 258) almost colourless crystals, soluble in water and alcohol, beginning to melt, with decomposition, at 90° , and consisting of $C_4H_8N_2S, I_2$. Like the corresponding bromo-derivative, this diiodide, on treatment with silver chloride, exchanged half its halogen for chlorine, yielding thereby the chloriodide, $C_4H_8N_2S, ClI$.

In repeating the former experiment, I added the calculated quantity of solid iodine, to allylthiourea, in alcoholic solution. Heat was evolved (this was checked by external cooling with water) and the iodine quickly dissolved, yielding a clear, brown solution; on concentrating, and allowing it to cool, it solidified to a mass of hard, brownish crystals, which when washed with benzene and spirit, became nearly white, and melted at $132\cdot5$ — $133\cdot5^{\circ}$ (corr.) to a reddish liquid.

There is so marked a divergence between this melting point, and that one given by Maly, that it was considered advisable to check the formula by analysis; figures, however, were obtained, agreeing with those required for the diiodo-addition product.

0.2036 gave 0.259 AgI, and 0.1262 BaSO₄; I = 68.73; S = 8.52.

$C_4H_8N_2SI_2$ requires I = 68.59; and S = 8.66 per cent.

The compound is readily soluble in water and alcohol, insoluble in benzene; its aqueous solution is sharply acid to litmus, gives the reaction for iodine, after the addition of chlorine water, and is not

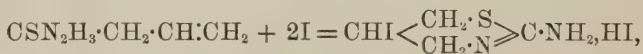
* This does not apply to compounds in which the bromine is included in an aromatic ring, such as bromophenylthiourea.

desulphurised, either by ammoniacal silver, or by alkaline lead salts, even on boiling.

Action of Caustic Alkali.—Ten grams of the di-iodide were dissolved in a little water, and the solution mixed with a slight excess of strong caustic potash; a dense, nearly colourless, very tenacious oil at once sank to the bottom. After a short time, the supernatant liquor was poured off and examined; it was found to contain much alkali iodide. The residual oil (washed with water) became pasty at -8° , but did not solidify; it was very sparingly soluble in water or dilute alkali, insoluble in ether, miscible with a little spirit, readily soluble in hydrochloric acid, strongly alkaline to test-paper, and reacted freely for iodine when treated with chlorine water. In this case, therefore, as in that of the corresponding bromo-compound, part of the halogen is removed by treatment with cold alkali, and part left in a basic residue. In order to get the latter in a form fit for analysis, it was dissolved in dilute hydrochloric acid, and picric acid added to the clear solution. The bright yellow, amorphous precipitate thus produced was collected, well washed with water, and dissolved in boiling alcohol; on cooling, the solution deposited spherical aggregates of orange-yellow, minute prisms, darkening at 172° , and melting, somewhat indistinctly, at $176-177^{\circ}$. If heated more strongly, it turns reddish-black, swells up, and effervesces, evolving violet fumes of iodine. It is practically insoluble in boiling water; the alcoholic solution, if mixed with starch and chlorine water, and then diluted, gives no blue coloration.

0.2094 gave 0.1032 AgI and 0.1057 BaSO₄. S = 6.94; I = 26.62. C₄H₇N₂SI, C₆H₅(NO₂)₃·OH requires S = 6.80; I = 26.92 per cent.

The interaction may be thus represented—



the iodised base, accordingly, being μ -amido- γ -iodopentthiazoline, otherwise β -iodotrimethylene- ψn -thiourea. When the base is treated with ammoniacal silver nitrate, a white precipitate forms, which is scarcely coloured, even by exposure to direct sunlight.

Iodine appears not to combine with allylthiocarbimide. With iodine monobromide interaction occurred, but no bromiodopropylthiocarbimide could be obtained.

ACTION OF ORGANIC BASES ON DIBROMOPROPYLTHIO-CARBIMIDE.

Numerous experiments were made in this direction, using primary and secondary bases, and phenylhydrazine. Interaction occurred

readily in every instance on warming, but the bases, when liberated from the corresponding hydrobromides by caustic alkali, were, very frequently, uninviting viscid masses, sometimes having the consistence of birdlime or pitch, and resisting all the attempts made to get them into suitable condition for analysis. The cases where definite results were attained are recorded below.

Dibromopropylthiocarbimide and Paratoluidine.

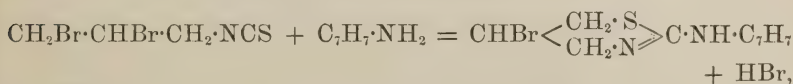
These, in molecular proportion, were separately dissolved in nearly absolute alcohol, the solutions mixed, and the alcohol driven off on the water bath. The residue, a thick, apparently uncrystallisable, acid syrup, consisting of the hydrobromide, was dissolved in dilute hydrochloric acid, and the clear, yellow solution treated with excess of caustic soda. The yellowish, heavy oil which was precipitated, in a short time changed to a whitish solid; the alkaline liquor poured off from this contained sodium bromide. The solid was twice recrystallised from alcohol, and thus obtained in rosettes of pointed, white prisms melting at 124–125° (corr.).

Analysis gave the following result.

0.2097 afforded 0.1743 BaSO₄. S = 11.42.

C₁₁H₁₃N₂SBr requires S = 11.24 per cent.

The interaction may be thus formulated—



the product being, accordingly, μ -paratolylamido- γ -bromopenthiazole, or, using the “thiourea” nomenclature, β -bromotrimethylene- ψn - ν -paratolylthiourea.*

The substance is very faintly alkaline to test-paper, freely soluble in warm alcohol, much less so in cold, insoluble in water. It is not affected by boiling with alkaline lead solution, and gives, with ammoniacal silver nitrate, a white, amorphous precipitate, which is not blackened by heating the mixture.

* Possibly, since thiocarbimide and a monosubstituted base are here interacting, the intermediate formation of a *thiocarbamide*, $\text{SC}\left\langle \begin{array}{c} \text{NH}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br} \\ \text{NHTo} \end{array} \right\rangle$,

might be anticipated, with subsequent break-down into $\text{SC}\left\langle \begin{array}{c} \text{NH}\cdot\text{CH}_2 \\ \text{NTTo}\cdot\text{CH}_2 \end{array} \right\rangle \text{CHBr}$ and HBr; but, in the first place, even if a thiocarbamide were initially produced, the deformation of its molecule into the “labile” (thiourea) configuration, under the influence of the halogen, is to be expected; and, secondly, a compound having the structure indicated, would almost certainly give up its sulphur without difficulty to ammoniacal silver nitrate.

μ-Orthotolylamido-γ-bromopenthiiazoline, $\text{CHBr} < \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$.

After numerous unsuccessful attempts to isolate this compound, the following method was found to answer. Orthotoluidine and the thiocarbimide, in molecular proportion, were dissolved in spirit, and the mixture slowly evaporated on the water bath, so as to expel most of the solvent. The residue, a thick, yellow syrup, was transferred to a flask, and distilled with steam until the distillate ceased to be turbid; the residue in the flask, a clear, colourless solution, mixed with traces of a dark oil, which refused to come over, was separated from the latter by filtration through paper, and the filtrate concentrated on the water bath. On cooling, the hydrobromide sank as a clear, pale brown oil, which showed no signs of solidifying even after some days' standing. It was then dissolved in a sufficiency of warm water containing a trace of spirit (about 20 volumes were required) and caustic potash added; the base was thereupon precipitated as a paste, which in a short time became tough. In this condition it was very freely soluble in boiling spirit, from which, on cooling, it was deposited in well-formed crystals; after a couple of recrystallisations from the same solvent, it formed beautiful, vitreous, apparently rhombic, plates, melting at $134\cdot5$ — $135\cdot5^\circ$ (corr.).

0.2039 gave 0.1672 BaSO_4 . $\text{S} = 11\cdot27$.

$\text{C}_{11}\text{H}_{13}\text{N}_2\text{SBr}$ requires $\text{S} = 11\cdot24$ per cent.

The orthotolyl base is feebly alkaline to litmus; when pure, it is somewhat sparingly soluble in boiling alcohol, much less so in cold, and insoluble in water. Its alcoholic solution, when treated with alkaline lead tartrate, is not desulphurised; even the whitish precipitate, which falls on the addition of ammoniacal silver nitrate, may be boiled without the least sign of darkening.

μβ-Naphthylamido-γ-bromopenthiiazoline, $\text{CHBr} < \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$.

By evaporating on the water bath mixed alcoholic solutions of dibromopropylthiocarbimide and β-naphthylamine, the hydrobromide was obtained as a tenacious, brownish syrup, difficultly soluble in cold water. It was dissolved in dilute hydrochloric acid, the solution mixed with excess of caustic alkali, and the precipitated free base, a thick, brown oil, washed with water, and set aside; after a few days it solidified, and by repeated recrystallisation from spirit, using animal charcoal, brilliant, nearly white, prisms were obtained, softening at 189° , and melting between 190 and 191° (corr.).

0.1992 gave 0.1430 BaSO_4 . $\text{S} = 9\cdot86$.

$\text{C}_{14}\text{H}_{13}\text{N}_2\text{SBr}$ requires $\text{S} = 9\cdot98$ per cent.

The base is neutral to litmus; slightly soluble in boiling water, easily in boiling alcohol, rather sparingly in cold; it is not visibly affected by boiling with alkaline solution of lead. Ammoniacal nitrate of silver precipitates a white, amorphous substance, not readily coloured by exposure to white light, and not blackened on boiling; this precipitate is insoluble in dilute nitric acid, but is decomposed by the concentrated acid, with formation of silver bromide.

μz-Naphthylamido-γ-bromopentthiazoline, $\text{CHBr} \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} \gg \text{C} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7$.

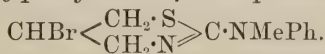
Operating as in the preceding case, an extremely viscid brown hydrobromide was obtained, practically insoluble in water; the base set free from the hydrochloric solution of the hydrobromide formed a tenacious paste, eventually acquiring a pitch-like consistence, it was insoluble in water, miscible with warm spirit, but did not crystallise from the latter. In a second experiment, the base was steam-distilled in order to remove any unchanged thiocarbimide or naphthylamine, but the product, even after long keeping, had solidified to only a trifling extent. For the purpose of analysis, the picrate was prepared, and purified by recrystallisation from boiling acetic acid. The myrtle-green prisms which separated on cooling were dissolved in hot hydrochloric acid; on partly neutralising the solution, the picrate was thrown down as a bright yellow powder.

0.2008 gave 0.0846 BaSO_4 . S = 5.80.

$\text{C}_{14}\text{H}_{13}\text{N}_2\text{SBr} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ requires S = 5.82 per cent.

The base, in alcoholic solution, is not desulphurised by boiling with alkaline lead tartrate; on the addition of ammoniacal nitrate of silver a white precipitate falls, not blackened by boiling, but changing rapidly in sunlight, first to rose colour, and then to deep purple. Dilute nitric acid, added to an alcoholic solution of the base, affords a rich, but evanescent, purple-blue coloration.

μ-Methylphenylamido-γ-bromopentthiazoline,



Interaction occurred spontaneously on adding the thiocarbimide to (alcoholic) methylaniline, with evolution of so much heat that the mixture began to boil. The blackish-brown syrup thus obtained was treated as described for the corresponding orthotolyl compound. After steam-distillation, the filtered residue was of a pale, claret colour; when concentrated and allowed to cool, it solidified to a slate-coloured, crystalline mass, becoming white on washing with spirit; by recrystallisation from hot water, small white prisms were ob-

tained melting at $183-184^{\circ}$ (corr.). The hydrobromide is very freely soluble in alcohol and in hot water, much more sparingly in cold; the solution has a marked tendency to remain supersaturated. Its aqueous solution reacts sharply acid, is not desulphurised by boiling with alkaline lead, or ammoniacal silver salts, and affords bromine when treated with chlorine water.

0.2001 gave 0.128 BaSO_4 . $S = 8.80$.

$\text{C}_{11}\text{H}_{13}\text{N}_2\text{SBr}\cdot\text{HBr}$ requires $S = 8.75$ per cent.

By mixing the aqueous solution with caustic potash, the base was thrown down as a heavy, brownish oil, which did not solidify in a freezing mixture; it is insoluble in water, soluble in alcohol, ether, benzene, and hydrochloric acid; the latter solution gives no reaction for bromine after treatment with chlorine water. Alcoholic silver nitrate precipitates a nearly white silver derivative; if this be covered with nitric acid, no immediate change takes place, but after a short time sudden and violent action occurs with evolution of nitrous fumes, silver bromide being left.



From the thiocarbimide, in alcohol, and piperidine: here, as with the other secondary base (methylaniline), vigorous action spontaneously occurred, the mixture boiling freely. On cooling, beautiful, anemone-like, crystalline tufts appeared, and the whole mass presently solidified; the product, after two recrystallisations from boiling spirit, formed brilliant, colourless, vitreous prisms, freely soluble in hot, but only sparingly in cold, alcohol, and melting at $189-190^{\circ}$ (corr.), with previous sintering at 188° . It dissolves also in cold water, yielding a solution which is neutral to litmus; this solution, when treated with chloroform and chlorine water, gives the reaction for bromine.

0.2588 gave 0.1792 BaSO_4 . $S = 9.51$.

$\text{C}_9\text{H}_{15}\text{N}_2\text{SBr}\cdot\text{HBr}$ requires $S = 9.31$ per cent.

The aqueous solution is not desulphurised by boiling with alkaline lead tartrate, but becomes clear yellow; with ammoniacal silver nitrate in excess, a bulky, white precipitate falls; the latter is very sensitive to light, a rich purple colour developing after a few seconds' exposure in the sun.

By adding dilute caustic potash, the free base was at once precipitated as a clear, almost colourless, strongly alkaline syrup, insoluble in water and alkali, soluble in alcohol, ether, and acids; it contains halogen, as shown by the copper oxide test, but does not react for it on treatment with chlorine water.

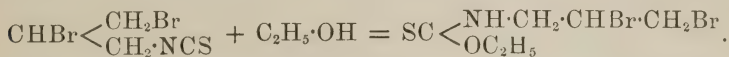
The alkalinity of the piperidyl base is so great as to allow of titration by standard acid; but on account of its practical insolubility in water, this is best performed indirectly.

0.3828 gram, dissolved in 20 c.c. N/10 HCl, required for neutralisation, 5.5 c.c. N/10 NaOH, corresponding to 14.5 c.c. acid used up to form the hydrochloride. Theory for $C_9H_{15}N_2SBr \cdot HCl$ requires 14.58 c.c.

ACTION OF ALCOHOLS ON THE THIOCARBIMIDE.

Dibromopropylthiocarbimide and Ethylic Alcohol. μ -Ethoxy- γ -bromopenthiazoline.

This reaction was carried out in the expectation of obtaining the sulphuretted urethane—



Eight grams of thiocarbimide, together with excess of anhydrous ethylic alcohol, were sealed up, and heated for about an hour, at a temperature slightly over 100° . On opening the tube, some gas escaped, smelling of mercaptan, and blackening lead paper; the contents of the tube thereupon partly crystallised. The mother liquor, from which the crystals had separated, was sharply acid to litmus, and contained hydrobromic acid. After two recrystallisations from hot alcohol, the solid was deposited in small, white prisms, melting at 96 — 97° (corr.); they were dried in a vacuum over sulphuric acid and analysed, with the following results.

0.2922 gave 0.3072 $BaSO_4$. S = 14.45.

0.225 „ 0.1893 $AgBr$. Br = 35.79.

Consequently, the thiourethane, which would require 10.5 of S and 52.4 of Br, had not been produced, but, as in the corresponding experiments with amines, the addition product, if formed at all, is unstable, and decomposes under the conditions of experiment, with elimination of the elements of hydrogen bromide, and production of a closed-chain compound.

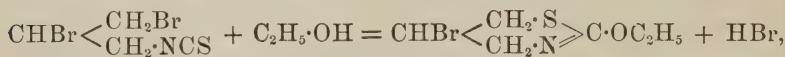
	Theory for $C_6H_{10}NSOBr$.	Experiment.
S.....	14.30	14.45
Br	35.67	35.79

The substance is moderately soluble in hot water, much less so in cold (the solution has a distinctly acid reaction to litmus), freely in boiling alcohol, but only sparingly at the ordinary temperature; it dissolves also in hydrochloric acid, from which it again separates on the

addition of dilute caustic alkali. It is not affected by boiling with alkaline lead tartrate, and gives no colour reaction with ferric chloride. Neutral, or ammoniacal, silver nitrate throws down a yellowish-white precipitate, which is decomposed by strong nitric acid, in the cold, with formation of silver bromide; this silver compound is remarkably sensitive to actinic light, rapidly changing in ordinary (diffused) daylight, through mauve and violet, to deep purple. On boiling, it is not desulphurised, but, on the contrary, whitens somewhat, thereby losing, to a great extent, its sensitiveness to light.

A very rough comparative experiment on the latter property was made, by adding silver nitrate to separate solutions of ammonium chloride and the substance, and exposing the resultant precipitates (Nos. 1 and 2 respectively) to dull daylight: In one minute, No. 2 began to colour, whilst No. 1 was yet not visibly affected; after seven minutes, a faint mauve coloration was perceptible in No. 1, No. 2, meanwhile, had acquired a strong purple colour.

Marked analogy appears to subsist between the action of dibromopropylthiocarbimide on the nitrogen bases, on the one hand, and ethylic alcohol on the other. In both cases, one-half of the thiocarbimidic bromine is eliminated in the form of hydrogen bromide; the failure of the alcohol derivative to desulphurise under the influence of lead, and especially of silver salts, points equally to the inclusion of sulphur as an integral member of an organic ring; and on the principle already mentioned, regarding the comparatively easy withdrawal of the end bromine atom, it is fairly safe to conclude that with respect to ring-closing also, the alcohol process runs a like course as in the case of the nitrogen bases (including ammonia). Accordingly, the interaction may be, at least provisionally, represented as follows.



the former product being the ethylic salt of β -bromotrimethylene- ψn -thiocarbamic acid or, more shortly, μ -ethoxy- γ -bromopenthi-
azoline.



This was obtained from the thiocarbimide and pure methylic alcohol by heating in a sealed tube for something over an hour at 110–115°; there was slight pressure on opening it, and a little hydrogen sulphide escaped, together with a fuming acid gas (HBr). The clear liquid product was evaporated to an oil, which, on rubbing with a glass rod, solidified; the solid was dissolved in hot, dilute spirit, and, on cooling, separated as a nearly white, crystalline mass, melting, without

decomposition, at 95—96°. Figures were obtained on analysis agreeing with those required for the methoxypentthiazoline.

0·2011 gave 0·180 AgBr. Br = 38·09.

0·2005 „ 0·2266 BaSO₄. S = 15·53.

C₅H₈NSOBr requires Br = 38·05; S = 15·26 per cent.

The methoxy-derivative is easily soluble in hot water and alcohol, rather sparingly in the cold. It is neither desulphurised by boiling with alkaline lead tartrate nor by ammoniacal silver nitrate; the latter precipitates a yellowish silver compound, whitening somewhat on standing in the dark, and, like the corresponding ethoxy-derivative, very sensitive to even dull, white light.

μ-Propoxy-γ-bromopentthiazoline, $\text{CHBr} \begin{smallmatrix} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{N} \end{smallmatrix} \text{C} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$.

Dibromopropylthiocarbimide and excess of normal propylic alcohol were heated together as in the preceding experiment; on cooling, the originally turbid mixture* had given place to a crystalline solid *plus* a clear liquid. There was no pressure on opening the tube, but the contents smelt of hydrogen sulphide, evolved a little acid vapour, and gave a strong acid reaction, due to hydrobromic acid. After three recrystallisations from spirit, the solid was obtained in white, pyramidal crystals, melting, without decomposition, at 96—97° (corr.).

0·2025 gave 0·2019 BaSO₄. S = 13·70.

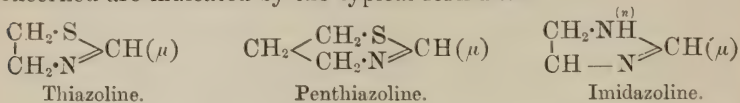
C₇H₁₂NSOBr requires S = 13·47 per cent.

μ-Propoxy-γ-bromopentthiazoline is moderately soluble in hot water, easily in hot spirit, rather sparingly in cold. Like its congeners, it is not desulphurised, either by boiling with alkaline lead solution, or by neutral or ammoniacal silver nitrate. The latter reagent throws down a yellowish, amorphous derivative, changing, on boiling, to white; insoluble in dilute nitric acid, but decomposed by warming with the concentrated acid, with formation of silver bromide: this silver compound also (unless boiled) is sensitive to light in a high degree, and changes rapidly to mauve even in very dull daylight. In a rude comparative experiment, similar to that with the ethoxy-compound, silver chloride was barely perceptibly altered in 10 minutes, the other silver derivative being then purple; in 15 minutes, when a faint bluish coloration was beginning to shew with the former, the latter had assumed a deep purple colour.

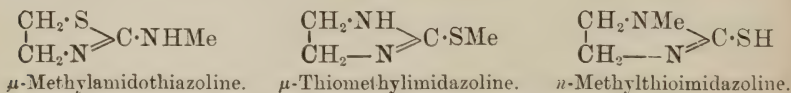
* The thiocarbimide dissolves tolerably freely in cold methylic alcohol, much less so in even anhydrous ethylic alcohol; in propylic alcohol it is rather sparingly soluble.

ADDENDUM.—*Imidazolines.*

The relations of the azoline compounds with which this paper is concerned are indicated by the typical formulæ—



Amongst thiazoline derivatives of the above type (apart from substitution in the carbon chain), μ -hydrogen is alone replaceable; the imidazolines, on the other hand, present two points where such replacement can occur, namely, $\text{CH}(\mu)$ and $\text{NH}(n)$. By the introduction into the latter, in either of these positions, of sulphuretted groups, forms can result, in which the sulphur is contained without the ring, and which are isomeric both with one another and with the thiazolines. Thus, for example, taking a methyl derivative as starting point, and assuming the substitution by a sulphur radicle to occur solely in the μ -position, one thio and two imidic forms are possible,



with two further possibilities if the n -hydrogen is in like manner replaced, or five isomers in all. The thio-compounds described below are imidazolines of the last-named, or n -, class, and were prepared

from the imidic base μ -methylimidazoline,* $\begin{array}{c} \text{CH}_2 \cdot \text{NH} \\ | \\ \text{CH}_2 - \text{N} \end{array} \gg \text{C} \cdot \text{CH}_3$.

μ -Methylimidazolylphenylthiourea, $\text{C}_6\text{H}_5 \cdot \text{N} : \text{C}(\text{SH}) \cdot \text{N} < \begin{array}{c} \text{C}(\text{CH}_3) \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \gg \text{N}$.

Phenylthiocarbimide and μ -methylimidazoline were separately dissolved in nearly anhydrous alcohol, and the solutions mixed; interaction commenced at once, with evolution of heat, and white crystalline matter quickly began to separate, the yield amounting to about 85 per cent. of that theoretically obtainable. On treating the product with boiling spirit, nearly the whole dissolved, leaving a trifling quantity of white, apparently amorphous, residue; the filtrate from the latter, when cool, deposited thick, lustrous, white prisms, which, after again recrystallising, melted at $173\text{--}174^\circ$ (corr.) to a yellowish clear liquid.

Analysis for sulphur afforded the following result.

* The material employed was a sample of "Lysidine," kindly supplied to me by Messrs. Jeyes; it is the 50 per cent. aqueous solution of the above base.

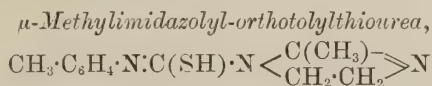
0.2059 gave 0.2184 BaSO₄. S = 14.58.

C₁₁H₁₃N₃S requires S = 14.62 per cent.

The compound is, accordingly, an addition-product of base and thiocarbimide; its formula is given above, and it may be named either *μ*-methylimidazolylphenylthiourea, or *n*-phenylthiouramido-*μ*-methylimidazoline.

It is slowly, and somewhat sparingly, soluble in hot water or alcohol, nearly insoluble in the cold, very sparingly in benzene, easily in cold, concentrated hydrochloric acid. Warm alkali dissolves it to a moderate extent, and the solution, when boiled with alkaline lead tartrate, is readily desulphurised; the alcoholic solution, when mixed with ammoniacal silver nitrate, blackens instantly.

Tertiary thioureas, so far as my experience goes, are either not desulphurised at all by alkaline lead tartrate, or else only with great difficulty, and after prolonged boiling; this and the following seem to be exceptional cases.



This compound was prepared from the base and orthotolylthiocarbimide, as described for the phenylic homologue; the yield of crude product amounted to 92 per cent. of the theoretical. By crystallising from spirit alone, the product was slightly brownish, but, after further treatment with spirit and animal charcoal, it was obtained in fine, white crystals, melting at 159—159.5° (corr.). The formula was checked by a sulphur determination.

0.2018 gave 0.202 BaSO₄. S = 13.76.

C₁₂H₁₅N₃S requires S = 13.74 per cent.

The compound is moderately soluble in water, freely so in boiling alcohol; it resembles generally the preceding compound in properties, the potash-solution, moreover, is desulphurised moderately readily by boiling with alkaline lead tartrate.

Ethyl- and allyl-thiocarbimides also combined with the base on warming; the products, in both cases, were sticky oils, which did not show any sign of solidification after long standing.

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IV.—*Studies of the Terpenes and Allied Compounds.* *New Derivatives from α -Dibromocamphor.*

By MARTIN ONSLOW FORSTER, Ph.D., First Salters Company's Research Fellow at the City and Guilds of London Institute Central Technical College.

Introductory.

THE behaviour of α -dibromocamphor towards nitric acid was studied more than 10 years ago by Kachler and Spitzer, who allowed a mixture of equal parts of concentrated and fuming acid to act on dibromocamphor during a protracted period (*Monatsh.*, 1883, **4**, 554); they recorded the formation of dinitrobromomethane, camphoronic acid, $C_9H_{12}O_5$, hydroxycamphoronic acid, $C_9H_{12}O_6$, and a small quantity of a crystalline substance melting at $87-88^\circ$, which may have the composition $C_{24}H_{33}BrN_4O_{12}$. From β -dibromocamphor and fuming nitric acid the same investigators obtained a nitro- β -dibromocamphor melting at 130° (*Monatsh.*, 1882, **3**, 218; **4**, 566).

In the hope that light would be thrown on the structural relationship existing between α -dibromocamphor and the β -modification, Dr. Armstrong suggested that an attempt should be made to obtain a nitro-derivative from the former, isomeric with nitro- β -dibromocamphor. On subjecting α -dibromocamphor to the action of fuming nitric acid (density 1.52), it was soon observed that a somewhat remarkable change takes place; the substance is rapidly dissolved by the acid, and at first the temperature falls, but then gradually rises spontaneously to about 70° , when dense, ruddy fumes are liberated in large volume. From the oily product, a crystalline substance is isolated without difficulty, in quantity amounting to about 10 per cent. of the material used; it is free from nitrogen, and has the composition $C_{10}H_{14}Br_2O_2$.*

The conditions which affect the production of this substance afford no clue to its chemical nature. A careful study of the derivatives to which it gives rise, however, reveals its lactonic character, the single oxygen atom by which its empirical formula differs from that of dibromocamphor appearing to enter the ring between the carbonyl group and one of the neighbouring carbon atoms. There is every

* In a preliminary notice of the investigation (*Proc.*, 1895, **4**), this substance was described as having the composition $C_{10}H_{12}Br_2O_2$. Study of its derivatives having shown that it must be represented by the formula $C_{10}H_{14}Br_2O_2$, the numbers required by this expression were calculated, and were found to agree more closely with the analytical results already announced (*loc. cit.*) than does the percentage composition of a substance having the formula $C_{10}H_{12}Br_2O_2$.

reason to suppose that the bromine atoms occupy relatively the same position as in α -dibromocamphor, it being unlikely that the formation of the new compound affords an instance of rebromination. as, although bromine is liberated in the course of the action, the presence of silver nitrate does not interfere with the production of the substance; moreover, addition of bromine to the nitric acid used, does not augment the yield. A noteworthy fact in connection with this change is the importance of using the strongest nitric acid procurable; in carrying out the investigation it has been customary to distil 500 c.c. of commercial fuming nitric acid (density 1.52) from 200 c.c. of concentrated sulphuric acid, the operation being interrupted when 400 c.c. has passed over. .

The dibromolactone obtained in the manner indicated gives rise to an interesting series of compounds, and before passing on to the experimental matter with which the present communication deals, it appears desirable to give a brief sketch of these substances, and the manner in which they are related to one another.

The properties of the initial compound are most characteristic. It crystallises very readily from organic solvents, forming long, prismatic needles melting at 152° ; cold, concentrated sulphuric acid has no action on it, and it may be crystallised from hot, fuming nitric acid. The substance is indifferent towards phenylhydrazine, aniline, benzoic chloride, acetic anhydride, and hydroxylamine, but is attacked by alkalis with great readiness. Thus alcoholic potash eliminates bromine, giving rise to a lactone of the formula $C_{10}H_{14}O_3$, which, under the influence of a boiling solution of barium hydroxide, yields the acid $C_{10}H_{16}O_4$, melting at 203° . As will be seen from its empirical formula, the lactone $C_{10}H_{14}O_3$ cannot be regarded as the substance of which the dibromolactone is a haloïd derivative, and this is also shown by the fact that, on brominating the lactone, only one atom of the halogen enters the molecule, a derivative of the composition $C_{10}H_{13}BrO_3$ being formed. It seems probable that the production of the lactone involves the displacement of bromine by hydroxyl groups, and the subsequent elimination of the elements of water.

Whilst alkalis eliminate both bromine atoms from the dibromolactone, only one is removed by reducing agents. Simultaneously, however, the lactone ring is split, and an unsaturated monobromocarboxylic acid is produced. This substance, which has the formula $C_{10}H_{15}BrO_2$, melts at 159° ; it forms well-defined salts, and has marked acidic characteristics, dissolving in a cold, aqueous solution of sodium carbonate, liberating carbon dioxide, and although but sparingly soluble in boiling water, the solution is distinctly acid towards litmus. Its unsaturated character is revealed by the behaviour of a solution containing sodium carbonate towards potassium

permanganate, which it immediately decolorises, and also by the readiness with which bromine dissolved in chloroform is decolorised when mixed with a solution of the acid in the same medium. The product of the latter change consists entirely of a dibromolactone, which it is to be supposed is formed by the elimination of hydrogen bromide from a tribromocarboxylic acid, incapable of existing in the free state. Fittig has shown that a similar behaviour towards bromine is characteristic of $\beta\gamma$ -unsaturated acids, which take up two atoms of the halogen, and at once part with hydrogen bromide, yielding a β -bromo- γ -lactone.

The behaviour of the monobromocarboxylic acid towards sulphuric acid affords further evidence in favour of the view that it is a $\beta\gamma$ -unsaturated acid. It is characteristic of these substances that, when subjected to the influence of sulphuric acid, they are converted into the isomeric lactones, the investigations of Fittig and his pupils having shown that this behaviour is generally manifest in the aliphatic series, but is not met with among aromatic compounds (*Ber.*, 1894, **27**, 2668). When this test is applied to the acid from camphor, it is found to be converted by sulphuric acid into an isomeride which crystallises in magnificent, lustrous plates, melting at $93-94^{\circ}$. It has the properties of a lactone, and, on hydrolysis, yields an acid free from bromine. The bromolactone is a saturated compound, being indifferent towards bromine, and fuming nitric acid has no action on it, whereas the isomeric bromocarboxylic acid readily yields a nitro-compound.

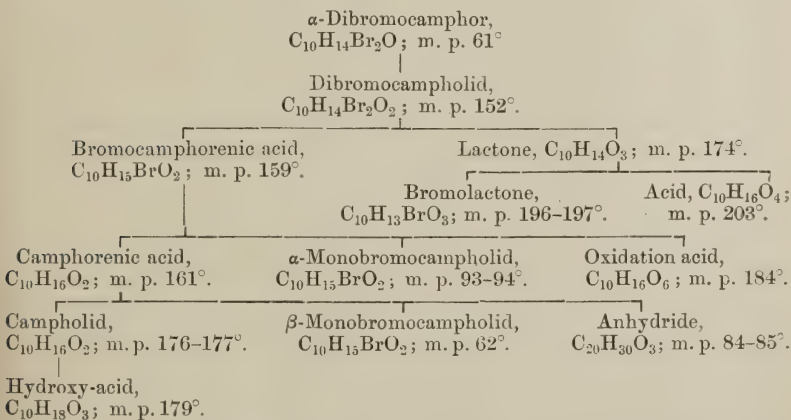
Although the halogen in the bromocarboxylic acid resists the action of such reducing agents as zinc and acetic acid, sodium and alcohol, or tin and hydrochloric acid, the bromine is completely eliminated when a solution of the sodium salt is submitted to prolonged treatment with sodium amalgam at the temperature of boiling water. The product, which has the formula $C_{10}H_{16}O_2$, melts at 161° , and exhibits the character of a $\beta\gamma$ -unsaturated acid. It dissolves in a cold aqueous solution of sodium carbonate, liberating carbon dioxide, and the solution in hot water is acid towards litmus; potassium permanganate is immediately decolorised when added to a cold, alkaline solution of the acid. The solution in chloroform at once decolorises bromine dissolved in the same medium, and hydrogen bromide is liberated, a monobromolactone of the composition $C_{10}H_{15}BrO_2$ being formed, which melts at 62° , and is isomeric with the bromolactone obtained directly from the bromocarboxylic acid.

When the carboxylic acid, $C_{10}H_{16}O_2$, is dissolved in concentrated sulphuric acid, it is transformed into an isomeric lactone which melts at $176-177^{\circ}$; it resembles camphor in appearance, has the odour of that substance, and sublimes slowly at 100° . Its properties are lac-

tonic, and it gives rise to an acid, $C_{10}H_{18}O_3$, which crystallises in lustrous needles, and melts at 179° .

Nomenclature.—The desirability of being in a position to refer without confusion to these substances has rendered necessary the adoption of some convenient system of nomenclature. On consideration of their empirical formulæ, it will be seen that the compounds in question arrange themselves into two classes, typified on the one hand by the carboxylic acid, $C_{10}H_{16}O_2$, formed from the bromocarboxylic acid obtained from the original dibromolactone by means of alcoholic ammonia and zinc dust, and on the other from the isomeric lactone to which the acid gives rise under the influence of concentrated sulphuric acid. It is proposed that reference be made to the new acid as *camphorenic acid*, a name which indicates, by the syllable *en*, the unsaturated nature of the substance. The isomeric lactone will be called *campholid*, the termination *olid* indicating, according to systematic nomenclature, a compound of lactonic character. The product of the action of fuming nitric acid on α -dibromo-camphor is, therefore, *dibromocampholid*, and the acid obtained on reducing this substance will be called *bromocamphorenic acid*. It is proposed to indicate the isomerism exhibited by the product of the action of sulphuric acid on bromocamphorenic acid, and the compound obtained from camphorenic acid and bromine, by referring to these substances as α -monobromocampholid and β -monobromocampholid respectively.

The generic relationship which runs through the new group of compounds will be, perhaps, more clearly illustrated by the following scheme, intended to represent the steps by which it is possible to pass from one compound to another.



In view of the relation between dibromocampholid and campholid

itself, it was to be expected that, when brominated, the latter would either give rise to the former, or become converted into one of the isomeric monobromo-derivatives. Campholid, however, is not attacked by bromine at 100° , and the two monobromo-derivatives are also indifferent towards the halogen; moreover, camphorenic acid and the sodium salt are converted by bromine into β -monobromocampholid, no trace of dibromocampholid being formed. When, however, the methylic salt of camphorenic acid is brominated, a mixture of mono- and dibromocampholid is formed. This is most likely owing to the effect produced on the neighbouring methenyl group by neutralising the carboxyl radicle. While this is free, bromination does not take place, and the halogen merely saturates the ethylenic linking, whereupon hydrogen bromide is eliminated, and this change leads to the formation of a monobromolactone; when, however, the carboxyl radicle is rendered inactive by the introduction of the methyl group, substitution occurs in the neighbouring methenylic residue at the same time, and the usual addition of bromine also takes place, the ethylenic linking becoming saturated, and this being followed by elimination of methylic bromide, the closing of the ring is effected, and a dibromolactone is formed.

Specific Rotatory Power.—The lactones and unsaturated acids with which the present communication deals, are all optically active, and their examination has afforded striking evidence of the alteration in rotatory power attending ring formation. It has been already observed in the case of several acids belonging to the sugar group that the formation of the lactone ring involves a very marked alteration in the behaviour towards polarised light; for instance, whilst gluconic acid has the specific rotatory power $[\alpha]_D = -1.74^{\circ}$ (*Annalen*, 1892, **271**, 78), the lactone has $[\alpha]_D = +68.2^{\circ}$ (*Ber.*, 1890, **23**, 2626), and mannosaccharic acid, which is very feebly active, forms a double lactone which has $[\alpha]_D = +201.8^{\circ}$ (*Ber.*, 1891, **24**, 541). It is, therefore, interesting to observe that the changes involved in the production of such lactones as campholid and its bromo-derivatives are also attended with radical alterations in specific rotatory power. With regard to campholid, whilst camphorenic acid has $[\alpha]_D = +179.4^{\circ}$ in chloroform, the isomeric lactone has $[\alpha]_D = +27.4^{\circ}$ in the same medium. Bromocamphorenic acid has, in chloroform, the specific rotatory power $[\alpha]_D = +144.1^{\circ}$, whilst the isomeric α -bromocampholid has $[\alpha]_D = +10.9^{\circ}$; β -bromocampholid, the formation of which involves elimination of hydrogen bromide from brominated camphorenic acid, has the specific rotatory power $[\alpha]_D = +3.5^{\circ}$ when dissolved in a certain proportion of chloroform, becoming inactive when the solution is more concentrated.

Although systematic investigation of the influence exerted by the

solvent on the specific rotatory power of these substances must be postponed for the present, experiment has shown that in the case of bromocamphorenic acid and β -bromocampholid, the use of benzene instead of chloroform is attended with a marked change in the rotation, and to a smaller extent dibromocampholid is affected in the same way. Thus the latter substance has $[\alpha]_D = +64.5^\circ$ in chloroform, a solution of identical concentration in benzene giving $[\alpha]_D = +69.8$. Bromocamphorenic acid has $[\alpha]_D = +144.1^\circ$ in chloroform, and $+161.3^\circ$ in benzene, whilst β -bromocampholid has $[\alpha]_D = +3.5^\circ$ in chloroform, and -21.2° in benzene. It would be possible to quote many instances of the influence on rotatory power which the nature of the medium exerts, for example, the recent observation of Herzfeld (*Ber.*, 1895, **28**, 440), regarding the specific rotatory power of octacetylmaltose, which has been determined in chloroform and benzene, and is found to be $[\alpha]_D = +61.0$ and $[\alpha]_D = +76.5^\circ$ in the respective media. Whilst in this instance it is merely degree of rotation which is affected, rare observations of alteration in sign have been recorded; thus Freundler (*Compt. rend.*, 1890, **117**, 556), determining the specific rotatory power of propylic diacetyltartrate, found $[\alpha]_D = +36.7^\circ$ in carbon bisulphide, and -2.6° in bromoform. The camphor series, moreover, affords a still more striking instance of this phenomenon. α -Nitrocamphor has the specific rotatory power $[\alpha]_j = -7.5^\circ$ in alcohol, and $[\alpha]_j = -140^\circ$ in chloroform, whilst in the case of the β -modification, the value of $[\alpha]_j$ is $+7.5^\circ$ in alcohol, and -7.5° in benzene.

EXPERIMENTAL.

Dibromocampholid, $C_{10}H_{14}Br_2O_2$.

One hundred grams of recrystallised α -dibromocamphor are placed in a capacious flask (80 oz.), and covered with 200 c.c. of the strongest fuming nitric acid. The temperature of the liquid is at first sensibly reduced, and gradually rises spontaneously to about 70° , at which point a violent action takes place, rendered evident by vigorous evolution of ruddy fumes, and the generation of much heat. When all action ceases, the liquid is allowed to cool; on pouring it into a large volume of cold water, a heavy, brown oil separates, which is washed two or three times with cold water, and subsequently agitated for about 10 minutes with boiling water. As a consequence of this treatment it becomes very viscous, and acquires a pale yellow colour; when freed from water it readily dissolves in twice its bulk of boiling spirit, and the liquid solidifies to a crystalline magma on cooling. After expressing the oily mother liquor, the residue is washed two or three times with cold alcohol, and then recrystallised

from the minimum quantity of boiling spirit. Dibromocampholid is thus obtained in magnificent, lustrous needles, which frequently attain to more than an inch in length; it melts at 152° .

The following results were obtained on analysis.

0.1419 gave 0.1918 CO_2 and 0.0560 H_2O . $\text{C} = 36.86$; $\text{H} = 4.35$.

0.2071 „ 0.2806 CO_2 and 0.0814 H_2O . $\text{C} = 36.95$; $\text{H} = 4.36$.

0.1044 „ 0.1203 AgBr . $\text{Br} = 48.84$.

0.1076 „ 0.1244 AgBr . $\text{Br} = 49.13$.

0.1854 „ 0.2133 AgBr . $\text{Br} = 49.20$.

$\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}_2$ requires $\text{C} = 36.81$; $\text{H} = 4.29$; $\text{Br} = 49.08$ per cent.

Although many attempts have been made to increase the yield of this substance by varying the conditions attending its formation, it has never been obtained in quantities exceeding in weight 11 per cent. of the material used. Thus it is found that the use of smaller quantities of dibromocamphor (5, 10 or 20 grams), or of a greater proportion of nitric acid, has no influence on the relative amount of the product, nor is the yield augmented on checking the vigour of the action by immersing the flask in cold water. If nitric acid, having a lower density than 1.52 be taken, no spontaneous rise of temperature is observed, and almost the whole of the dibromocamphor can be easily recovered from the oil obtained on pouring the solution into cold water.

As it appeared not unlikely that the formation of the compound involved a liberation of bromine and the consequent bromination of an intermediate product, finely powdered silver nitrate was dissolved in the strongest fuming nitric acid, which was then allowed to act on α -dibromocamphor. Silver bromide was obtained in quantity representing 30 per cent. of the halogen available, but the yield of dibromocampholid was unaltered; when, moreover, 20 c.c. of bromine was added to the quantity of nitric acid usually taken, action proceeded in the ordinary manner, but no increase in yield was observed.

Dibromocampholid is insoluble in water, and scarcely soluble in cold alcohol, but dissolves in the boiling solvent, and also in ether, chloroform, petroleum, acetone, and glacial acetic acid; it crystallises from ethylic acetate in magnificent, long, transparent prisms, belonging to the orthorhombic system. It sublimes at a high temperature, and is somewhat volatile in an atmosphere of steam. The compound is indifferent towards bromine, and dissolves in concentrated sulphuric and fuming nitric acids without undergoing change, crystallising from the latter in long, transparent needles. It is in many respects a remarkably inert substance, and crystallises unaltered from boiling aniline, phenylhydrazine, acetic anhydride, or benzoic chloride; when it is heated, however, with an aqueous solu-

tion of sodium carbonate and alcohol, bromine is removed; and the halogen is also eliminated when the substance is heated for some time with a mixture of equal parts of nitric acid (density 1.42) and water. Dibromocampholid undergoes no change when the solution in glacial acetic acid is boiled for several hours with hydroxylamine hydrochloride.

The specific rotatory power of a solution containing 1.0269 grams in 25 c.c. of chloroform was determined in a 2-decimetre tube at 11° ; the mean of six concordant readings gave $\alpha_D = +5^{\circ} 18'$, whence $[\alpha]_D = +64.5^{\circ}$. It has been already stated that the influence which the nature of the solvent exerts on the rotatory power of dibromocampholid is more feeble than in the case of β -bromocampholid and bromocamphorenic acid; a solution in benzene of the above concentration gave $\alpha_D = +5^{\circ} 40'$ at 15° , whence $[\alpha]_D = +69.8^{\circ}$.

Hydrolysis of Dibromocampholid.

It has been already mentioned that elimination of halogen from dibromocampholid is readily effected by alkalis. The result of treatment with alkaline hydrolytic agents is the production of an acid having the formula $C_{10}H_{16}O_4$, the lactone $C_{10}H_{14}O_3$ being obtained as an intermediate product, in quantity varying according to the experimental conditions. Alcoholic potash is the agent most favourable to the formation of the lactone, whilst aqueous solutions of barium and sodium hydroxide give rise almost exclusively to the acid; the action of these alkalis on dibromocampholid will be therefore described in the order named.

Action of Alcoholic Potash on Dibromocampholid.—Twenty grams of the finely powdered substance are covered with about 50 c.c. of boiling alcohol, and heated for three hours in a reflux apparatus with 23 c.c. of an aqueous, 50 per cent. solution of caustic potash, which is added to the alcoholic liquid in small quantities at a time. The substance gradually dissolves, and the alkalinity produced by each fresh addition of potash is allowed to disappear before any more is added. The clear, red liquid, which is faintly alkaline, is allowed to cool, filtered from the potassium bromide which crystallises out along with unaltered substance (about 0.5 gram), reduced to small bulk by evaporation, and set aside for 48 hours. The crystalline substance which separates during this time is freed from oil, washed two or three times with cold petroleum, and recrystallised from hot alcohol; it is thus obtained in lustrous plates, and melts at 174° . From the analytical results, it will be seen that the compound has the formula $C_{10}H_{14}O_3$.

0.1703 gave 0.4097 CO_2 and 0.1183 H_2O . $\text{C} = 65.60$; $\text{H} = 7.71$.

0.1227 „ 0.2946 CO_2 and 0.0839 H_2O . $\text{C} = 65.48$; $\text{H} = 7.60$.

$\text{C}_{10}\text{H}_{14}\text{O}_3$ requires $\text{C} = 65.93$; $\text{H} = 7.68$ per cent.

A solution of 1.1826 grams in 25 c.c. of chloroform was examined at 15° in a 2-decimetre tube; the rotation $\alpha_D = -11^\circ 6'$, whence $[\alpha]_D = -117.3^\circ$.

The lactone is somewhat soluble in cold water, from which it crystallises in thick, transparent prisms; it fuses to an oil in boiling water, which dissolves it readily, forming a neutral solution. Although insoluble in cold alkalis, it dissolves readily when the solution is boiled, and no precipitate is formed on acidifying the cold liquid; it crystallises unchanged from boiling, aqueous ammonia. Phenylhydrazine has no action on it, and it is indifferent towards boiling acetic anhydride.

The bromo-derivative, $\text{C}_{10}\text{H}_{13}\text{BrO}_3$, is obtained by the action of bromine on the lactone. When the dry substance is covered with the halogen, no change takes place at first, but after remaining in contact for about a minute, action occurs quite suddenly, hydrogen bromide being liberated. The solid product is treated with sulphurous acid, washed several times with cold water, and finally crystallised from a considerable quantity of boiling alcohol, which deposits it, on cooling, in slender, lustrous needles melting at $196\text{--}197^\circ$. The following results were obtained on analysis.

0.1406 gave 0.2375 CO_2 and 0.0657 H_2O . $\text{C} = 46.06$; $\text{H} = 5.18$.

0.1460 „ 0.1062 AgBr . $\text{Br} = 30.91$.

$\text{C}_{10}\text{H}_{13}\text{BrO}_3$ requires $\text{C} = 45.98$; $\text{H} = 4.98$; $\text{Br} = 30.65$ per cent.

The bromolactone does not dissolve in water; it is insoluble in cold alkalis, but dissolves when the solution is boiled, and no precipitate is formed on acidifying the cold liquid. The halogen is eliminated on treatment with hot, alcoholic ammonia and zinc dust.

Hydrolysis of the Lactone.—2.5 grams of the lactone were heated in a reflux apparatus for an hour with 40 c.c. of aqueous barium hydroxide containing 3 grams of the crystallised hydrate. A current of carbonic anhydride was passed through the filtered liquid, and, after being boiled for a few minutes, the solution was freed from barium carbonate by filtration, and evaporated on the water bath until crystals began to separate; the substance thus obtained is the barium salt of the acid $\text{C}_{10}\text{H}_{16}\text{O}_4$, which is more conveniently obtained in the manner about to be described.

Action of Barium Hydroxide on Dibromocampholid.—The finely powdered substance is treated with successive quantities of a boiling, concentrated solution of barium hydroxide, in a flask provided with a reflux condenser; as long as any of the substance remains

undissolved, the alkalinity produced by a fresh portion of the hydrate is destroyed on boiling the liquid for a few minutes. When a clear solution is obtained, it is allowed to cool, filtered from a small quantity of unaltered dibromocampholid, reduced to a small bulk by evaporation in an open basin, cooled, and, after acidification with concentrated hydrochloric acid, repeatedly extracted with ether. On evaporating the ether, after agitating the solution with fused calcium chloride, a pale yellow substance is obtained, which crystallises from a mixture of ether and petroleum in minute, transparent rhombohedra, and melts, evolving gas, at 203° . The following results were obtained on analysis.

0.1716 gave 0.3742 CO_2 , and 0.1312 H_2O . $\text{C} = 59.47$; $\text{H} = 8.49$.

$\text{C}_{10}\text{H}_{16}\text{O}_4$ requires $\text{C} = 60.00$; $\text{H} = 8.00$ per cent.

The acid is very readily soluble in cold water, forming a strongly acid solution, which dissolves potassium carbonate with evolution of carbon dioxide; the alkaline liquid immediately decolorises a cold solution of potassium permanganate. It is extremely soluble in alcohol, chloroform, ethylic acetate, and organic solvents generally, excepting petroleum, in which it is insoluble. A solution in chloroform does not decolorise bromine, but on boiling the liquid a violent disengagement of hydrogen bromide occurs, and a colourless *dibromo*-derivative is formed, which crystallises from alcohol in feathery aggregates, and melts at $159\text{--}160^{\circ}$; this substance is insoluble in cold alkalis.

The *barium* salt is obtained by dissolving barium carbonate in a hot, aqueous solution of the acid; it is also formed on hydrolysing the lactone, $\text{C}_{10}\text{H}_{14}\text{O}_3$, with aqueous barium hydroxide. The solution is evaporated until the salt separates in white needles; the crystals are collected, washed with alcohol, and dried at 100° .

0.1501 gave 0.0641 BaSO_4 . $\text{Ba} = 25.11$.

0.1512 „ 0.0642 BaSO_4 . $\text{Ba} = 24.97$.

$(\text{C}_{10}\text{H}_{15}\text{O}_4)_2\text{Ba}$ requires $\text{Ba} = 25.60$ per cent.

The barium salt is very soluble in cold water, but is insoluble in alcohol, acetone, and ethylic acetate; the aqueous solution has an intensely bitter taste.

Action of Sodium Hydroxide on Dibromocampholid.—The substance dissolves slowly in a boiling aqueous solution of sodium hydroxide, and, on evaporating the filtered liquid, rendering acid with concentrated hydrochloric acid, and extracting several times with ether, the foregoing acid, $\text{C}_{10}\text{H}_{16}\text{O}_4$, is obtained on evaporating the solvent. If, however, the action of sodium hydroxide be allowed to proceed for a few minutes only, and the filtered liquid be extracted with ether

previous to acidification, the lactone, $C_{10}H_{14}O_3$ (m. p. 174°), is obtained.

An attempt was made to hydrolyse dibromocampholid by means of dilute sulphuric acid. The powdered substance was treated with boiling sulphuric acid (2 parts of concentrated acid in 10 parts of water) for six hours in a flask provided with a reflux condenser, but the greater part of the substance remained undissolved, and when recrystallised from alcohol melted at 152° .

Bromocamphorenic acid, $C_{10}H_{15}BrO_2$.

Fifty grams of dibromocampholid are covered with about 100 c.c. of boiling alcohol in a capacious flask, and to the liquid are added successively small quantities of zinc dust, and strong, aqueous ammonia, the temperature being maintained meanwhile on the water bath, until a portion of the clear, ammoniacal solution no longer becomes turbid when diluted with water. The liquid is then decanted from undissolved zinc, largely diluted with water, and finally acidified with dilute sulphuric acid, when a white, flocculent precipitate immediately separates; this is collected, washed several times with cold water, and dissolved in a small quantity of hot spirit, from which it crystallises in thin, lustrous plates. It frequently happens that on diluting the ammoniacal liquid, a yellowish-white, granular precipitate is thrown down; this consists of the zinc salt, which is invariably produced when the solution remains in contact with hot ammonia and zinc dust for a period longer than that necessary for reduction. In this case, the product is washed with cold water, and dissolved in dilute caustic soda, the solution being then precipitated with sulphuric acid.

The bromocarboxylic acid is readily soluble in cold alcohol, from which it crystallises in transparent, six-sided plates, melting at 159° ; it dissolves readily in organic solvents, separating in well-formed crystals from glacial acetic acid and petroleum. It is insoluble in cold water, but dissolves sparingly on boiling, forming an acid solution; it is volatile in an atmosphere of steam, and sublimes at a high temperature. Analysis gave the following results.

0.1685 gave 0.3016 CO_2 , and 0.0922 H_2O . C = 48.81; H = 6.08.

0.1152 „ 0.0877 AgBr. Br = 32.35.

0.1175 „ 0.0897 AgBr. Br = 32.44.

$C_{10}H_{15}BrO_2$ requires C = 48.58; H = 6.07; Br = 32.38 per cent.

A solution of 1.0060 gram in 25 c.c. of chloroform at 11° gave a rotation $\alpha_D = +11^\circ 36'$, this being the average of seven concordant readings; the specific rotatory power is, therefore, $[\alpha]_D = +144.1^\circ$. Dilution of the liquid appears to be without influence on the specific

rotatory power, as a solution containing 0.7247 gram in 25 c.c. of chloroform at 14° gave a rotation $\alpha_D = +8^{\circ} 22'$; this corresponds with a specific rotatory power $[\alpha]_D = +144.3^{\circ}$, a result sufficiently close to the one already given to show the constancy of this property between the limits indicated. The influence exerted by the nature of the medium is revealed when benzene is used as a solvent; a solution containing 0.7850 gram of bromocamphorenic acid in 25 c.c. of benzene at 15° gave a rotation $\alpha_D = +10^{\circ} 8'$, whence $[\alpha]_D = +161.3^{\circ}$.

The acid dissolves readily in cold alkalis, and it is also soluble in a cold, aqueous solution of sodium carbonate, carbon dioxide being liberated. No coloration is developed when ferric chloride is added to the dilute alcoholic solution, and it is indifferent towards Fehling's solution; the alkaline solution immediately decolorises potassium permanganate. The substance may be heated for an hour with boiling aniline without undergoing change, and a boiling alcoholic solution of sodium ethoxide has no action on it; when boiled during three hours with an aqueous solution of caustic soda, it is precipitated unchanged on adding acid, and silver nitrate produces no turbidity in the filtrate. A solution in chloroform immediately decolorises bromine in the same medium, and on evaporating the solvent dibromocampholid is obtained; the latter is also formed when bromine is added to the dry solid, much heat being generated, and hydrogen bromide evolved. Bromocamphorenic acid undergoes no change when allowed to remain for many days in contact with glacial acetic acid saturated with hydrogen bromide. The acid is indifferent towards hydroxylamine, benzoic chloride, and acetic anhydride, and undergoes no change when heated in a sealed tube with ammonia (sp. gr. 0.880) for five hours at 170° .

Monobromocamphorenic acid may be also prepared by reducing dibromocampholid with zinc dust and glacial acetic acid. The following salts have been obtained.

The *barium* salt is prepared by dissolving the acid in the minimum quantity of an aqueous solution of barium hydroxide, and evaporating the liquid till crystals form. It separates from the concentrated solution in lustrous plates, and in nodular aggregates when slowly deposited. From a specimen dried at 100° , the following analytical results were obtained.

0.2535 gave 0.0890 BaSO_4 . Ba = 20.64.

0.1963 „ 0.0706 BaSO_4 . Ba = 20.64.

$(\text{C}_{10}\text{H}_{14}\text{BrO}_2)_2\text{Ba} + 2\text{H}_2\text{O}$ requires Ba = 20.60 per cent.

On analysing the same preparation dried at 130° ,

0.2003 gave 0.0733 BaSO_4 . Ba = 21.52.

0.2148 „ 0.0796 BaSO_4 . Ba = 21.79.

$(\text{C}_{10}\text{H}_{14}\text{BrO}_2)_2\text{Ba}$ requires Ba = 21.78 per cent.

The *silver* salt is obtained by adding a slight excess of silver nitrate to an aqueous solution of the crystallised barium salt. The colourless precipitate is washed successively with water, alcohol, and ether, and dried at 50°. It is sparingly soluble in water, and dissolves with difficulty in boiling alcohol, from which it crystallises in lustrous needles. The dry salt darkens very slowly on exposure to light, but quickly blackens when treated with boiling water; it does not explode when heated suddenly. Analysis gave the following results.

0.2294 (precipitated) gave 0.1211 AgBr. Ag = 30.30.

0.0652 (crystallised) „ 0.0346 AgBr. Ag = 30.46.

$C_{10}H_{14}BrO_2Ag$ requires Ag = 30.50 per cent.

The *zinc* salt is obtained as a yellowish, granular precipitate when an alcoholic solution of the acid is boiled for some time with ammonia and zinc dust; it is also produced on adding an aqueous solution of zinc chloride to a neutral solution of the ammonium salt. The zinc salt is scarcely soluble in water, and but sparingly soluble in cold alcohol; it is more readily soluble in hot alcohol, and crystallises from acetone in tufts of minute, transparent needles. On adding water to the hot, alcoholic solution, and allowing the liquid to cool, the salt is obtained in stumpy prisms. It dissolves in alkalis, the solutions yielding the acid when acidified. When heated at 130—140°, the salt yields a colourless, crystalline sublimate of the acid. This behaviour is explained by its composition, which analysis shows to be represented by the formula $(C_{10}H_{14}BrO_2)_2Zn + C_{10}H_{15}BrO_2$.

0.2626 gave 0.0274 ZnO. Zn = 8.35.

$(C_{10}H_{14}BrO_2)_2Zn + C_{10}H_{15}BrO_2$ requires Zn = 8.08 per cent.

$(C_{10}H_{14}BrO_2)_2Zn$ requires Zn = 11.67 per cent.

The *ammonium* salt exists only in dilute, aqueous solution; if this is evaporated, or saturated with carbon dioxide, the salt is decomposed, and the acid separates.

The *copper* salt is obtained by adding copper sulphate dissolved in water to the neutral, aqueous solution of the ammonium salt, a bluish-green, flocculent precipitate being formed; when this is boiled with alcohol, a green solution is produced, and on adding a small quantity of water to the hot liquid and allowing it to cool, minute green needles are deposited.

The *methylic* salt is not formed when a solution of the acid in methylic alcohol is saturated at common temperatures with hydrogen chloride. It is prepared by dissolving 3 grams of the acid in a boiling solution of sodium methoxide in methylic alcohol containing 0.3 gram of sodium, and adding small quantities of methylic iodide until a few drops of the liquid, when diluted with water, no longer yield a

solid precipitate on acidification. The excess of methylic iodide having been removed, the liquid is diluted with water, and the colourless oil which is thrown down is washed two or three times with cold water, and extracted with ether; after being dried with calcium chloride, the solvent is evaporated, and the residual oil distilled. It boils at 255° under a pressure of 767.5 mm. The salt was analysed with the following result.

0.1792 gave 0.3379 CO_2 and 0.1078 H_2O . C = 51.4; H = 6.7.

$\text{C}_{10}\text{H}_{14}\text{BrO}_2\cdot\text{CH}_3$ requires C = 50.5; H = 6.5 per cent.

The methylic salt is a colourless, somewhat viscous oil, heavier than water, having a fragrant odour suggestive of camphor; it is volatile in an atmosphere of steam, the vapour being pungent and exhilarating. The salt is hydrolysed when heated with boiling alcoholic potash for six hours; it burns on platinum foil with a luminous, smoky flame, leaving no residue. The solution in chloroform immediately decolorises bromine, and, on evaporating the liquid, dibromocampholid is left.

Oxidation of Bromocamphorenic acid.

It has been already stated that the acid dissolved in an aqueous solution of sodium carbonate immediately decolorises potassium permanganate; an attempt was therefore made to obtain an oxidation product by means of this agent.

Twenty grams of finely powdered bromocamphorenic acid was suspended in 200 c.c. of boiling water, sodium carbonate being added until a clear solution was obtained; the liquid was then cooled to about 0° and mixed with an ice-cold, 2 per cent. solution of potassium permanganate, which was added in portions of 100 c.c. Crushed ice was also added to the liquid in order to maintain the temperature at 0° , and when 1,500 c.c. of the permanganate solution (corresponding to more than twice the molecular proportion) had been added, the liquid was allowed to remain for an hour surrounded with melting ice. After the removal of manganese dioxide, the clear liquid was concentrated to 200 c.c., acidified with concentrated hydrochloric acid, and the yellow solution extracted several times with ether. The pink syrup left on evaporating the united extracts rapidly solidified on being rubbed with a glass rod; the product was washed with hot ethylic acetate, and the colourless, insoluble portion dissolved in ether, which, when mixed with the same bulk of ethylic acetate, deposited the substance in groups of brilliant transparent prisms. The compound melts and evolves gas at 184° , and, after having been allowed to cool, melts at $84\text{--}85^{\circ}$; a specimen of the fused substance, however, after recrystallisation from dilute alcohol, melted at 184° .

0.1594 gave 0.3018 CO₂ and 0.0988 H₂O. C = 51.63; H = 6.85.

0.1559 „ 0.2967 CO₂ and 0.0944 H₂O. C = 51.91; H = 6.73.

C₁₀H₁₆O₆ requires C = 51.72; H = 6.90 per cent.

The oxidation product has the properties of a dibasic acid; it is strongly acid towards litmus, dissolves readily in alkalis, and with effervescence in alkali carbonates, and the aqueous solution. It dissolves readily in cold alcohol and ether, being but sparingly soluble in cold ethylic acetate; the solution in boiling water deposits rosettes of minute, transparent prisms as the liquid cools.

The *silver* salt was obtained as a pale yellow precipitate on adding silver nitrate in slight excess to a neutral solution of the ammonium salt; after being collected and washed successively with water, alcohol, and ether, the salt was dried in the desiccator. It darkens when exposed to light, or when heated for a few minutes in the water oven; there is no explosion when the salt is suddenly heated. Probably owing to the unstable character of the salt, which gradually darkens even in a desiccator protected from light, analysis of the substance gave somewhat unsatisfactory results, which seem to indicate, however, that the acid contains two carboxylic groups.

0.1402 gave 0.0726 Ag. Ag = 51.78.

0.1926 „ 0.0998 Ag. Ag = 51.87.

C₁₀H₁₄O₆Ag₂ requires Ag = 48.65 per cent.

C₁₀H₁₃O₆Ag₃ „ Ag = 58.58 „

α-Monobromocampholid, C₁₀H₁₅BrO₂.

In the introduction, it was mentioned that bromocamphorenic acid shows the behaviour which aliphatic $\beta\gamma$ -unsaturated acids exhibit, when brought in contact with sulphuric acid, undergoing molecular rearrangement, and being converted into the isomeric lactone.

Finely divided bromocamphorenic acid is added in small quantities at a time to five times its weight of concentrated sulphuric acid, which is continuously stirred during the operation. Heat is developed, the substance gradually becoming dissolved, and when a clear solution is obtained, the pale brown liquid is poured into a large volume of cold water; a white, crystalline precipitate at once separates, and this is collected, and washed several times with cold water. If the substance is added too quickly to the acid, liberation of a small quantity of hydrogen bromide is observed, but this may be avoided by preventing a sudden rise in the temperature of the liquid. The lactone crystallises from hot alcohol in magnificent, lustrous plates, separating from concentrated solutions in long, slender needles; it melts at 93–94°.

0.1575 gave 0.2805 CO_2 and 0.0878 H_2O . $\text{C} = 48.57$; $\text{H} = 6.19$.

0.1537 „ 0.1183 AgBr . $\text{Br} = 32.71$.

$\text{C}_{10}\text{H}_{15}\text{BrO}_2$ requires $\text{C} = 48.58$; $\text{H} = 6.07$; $\text{Br} = 32.38$ per cent.

The compound dissolves readily in organic solvents, and is soluble in boiling water, from which it separates as the liquid cools; it may be conveniently crystallised from a mixture of petroleum and alcohol, being obtained from this medium in thin, lustrous plates. It is volatile in an atmosphere of steam.

Apart from its neutral character, the properties of α -monobromocampholid differ very widely from those of bromocamphorenic acid. The lactone is insoluble in cold alkalis, and dissolves in bromine without undergoing change; it is indifferent towards a boiling mixture of glacial acetic and fuming nitric acids, whilst this treatment converts bromocamphorenic acid into a nitro-compound. Potassium bromide separates immediately when a concentrated, aqueous solution of caustic potash is added to the boiling solution in alcohol, the original acid, in boiling alcoholic solution, being indifferent towards metallic sodium. So easily is bromine eliminated from the lactone that, on digesting it for a considerable period with boiling water, and filtering the cold liquid, a precipitate is at once formed on adding silver nitrate to the acidified solution.

The conversion of bromocamphorenic acid into the isomeric lactone is attended with a remarkable alteration in the specific rotatory power. A solution of 0.9549 gram of α -bromocampholid in 25 c.c. of chloroform was examined in a 2-decimetre tube at 21° ; a rotation $\alpha_D = +0^\circ 50'$ was observed as the mean of seven concordant readings, whence $[\alpha]_D = +10.9^\circ$.

Hydrolysis of α -Monobromocampholid.—The lactonic character of the substance is revealed on treatment with an aqueous solution of barium hydroxide. After remaining in contact with the boiling agent in a reflux apparatus for three hours, the lactone becomes dissolved, and the alkalinity of the liquid is gradually destroyed; on evaporating the solution which has been cooled and filtered, a *barium* salt crystallises in prismatic needles. It was dried at 130° for half an hour, and analysed with the following result.

0.1320 gave 0.0611 BaSO_4 . $\text{Ba} = 27.21$.

$(\text{C}_{10}\text{H}_{15}\text{O}_3)_2\text{Ba}$ requires $\text{Ba} = 27.23$ per cent.

On acidifying a solution of the barium salt, the *acid* is obtained as a colourless, viscous oil, which rapidly becomes hard and crystalline. It separates from a mixture of petroleum and ethylic acetate in transparent prisms, and melts at 195° ; it is very readily soluble in water, alcohol, ether, and acetic acid, but is insoluble in petroleum. The aqueous solution dissolves sodium carbonate with effervescence

the liquid having no reducing action on ice-cold potassium permanganate.

Camphorenic acid, $C_{10}H_{16}O_2$.

Bromocamphorenic acid is readily attacked by sodium amalgam, especially at slightly elevated temperatures.

Fifty grams are suspended in 200 c.c. of boiling water and vigorously agitated during the addition of 4 per cent. sodium amalgam in small quantities. It is necessary that the liquid should remain at the temperature of boiling water, otherwise the reduction is incomplete, and a mixture of the new compound with unaltered substance is obtained; as the separation of the latter is extremely tedious, the observance of this precaution is of some importance. For the quantity mentioned, about 500 grams of amalgam will be found sufficient, and when this amount has been added, if a drop of the liquid becomes solid when placed on a watch glass, it is decanted from the mercury and allowed to cool. The paste of fibrous needles thus obtained, consisting of the sodium salt of the reduction product, is collected, the alkaline liquid being removed by filtering through asbestos. On dissolving the salt in water, and adding dilute sulphuric acid, a white, flocculent precipitate is formed, which is collected and washed thoroughly with cold water. In order to completely remove the last traces of the original substance, the precipitated carboxylic acid is again agitated with 50 grams of sodium amalgam, the separation and decomposition of the sodium salt being repeated; as the latter only crystallises from strongly alkaline solutions, it is generally found necessary after this supplementary treatment with the amalgam to add sodium carbonate to the hot liquid until the sodium salt begins to separate. The acid, on being crystallised from hot alcohol, separates in long, slender needles; it melts at 161° .

0.1500 gave 0.3925 CO_2 and 0.1314 H_2O . $C = 71.36$; $H = 9.73$.

$C_{10}H_{16}O_2$ requires $C = 71.43$; $H = 9.52$.

The substance is very soluble in organic solvents, and dissolves to some extent in boiling water, being insoluble in the cold; it crystallises from ether in transparent prisms which become opaque in the water oven. It is volatile in an atmosphere of steam, and sublimes when heated, the vapour having a faint, camphor-like odour.

A solution of 1.1840 gram in 25 c.c. of chloroform was examined in a 2-decimeter tube at 18° ; it exhibited a rotation of $\alpha_D = +17^\circ$, and the specific rotatory power is, therefore $[\alpha]_D = +179.4^\circ$. The substance dissolves readily in cold, aqueous alkalis, and in a cold solution of sodium carbonate, carbon dioxide being evolved; the solution in hot water is acid, and potassium permanganate is immedi-

ately decolorised when added to the cold solution containing sodium carbonate. Boiling acetic anhydride has no action on the acid, which is also indifferent towards benzoic chloride.

The *sodium* salt, which separates from a strongly alkaline solution in tough, fibrous masses, is extremely soluble in water, and may be recrystallised from ethylic acetate, separating from this solvent in lustrous, silky needles; a specimen obtained in this way was analysed with the following result.

0.2395 gave 0.0948 Na_2SO_4 . $\text{Na} = 12.82$.

0.2940 „ 0.1161 Na_2SO_4 . $\text{Na} = 12.79$.

$\text{C}_{10}\text{H}_{15}\text{O}_2\text{Na}$ requires $\text{Na} = 12.10$ per cent.

The somewhat unsatisfactory character of these numbers is most probably due to slight decomposition taking place at the temperature of boiling ethylic acetate, as the crystallised salt does not redissolve completely in that solvent, and the solution in cold water is strongly alkaline.

The *zinc* salt resembles that of bromocamphorenic acid; it is obtained on adding zinc chloride dissolved in water to a neutral solution of the ammonium salt.

The *methylic* salt is not formed when a solution of the acid in methylic alcohol is saturated at common temperatures with hydrogen chloride, but it can be prepared by dissolving the sodium salt in methylic alcohol and heating the solution with methylic iodide for several hours in a reflux apparatus; on diluting the liquid with water, and extracting with ether, a colourless oil is obtained which boils at 215° under a pressure of 767.5 mm. It is viscous, and heavier than water, and burns on platinum foil with a luminous, smoky flame, leaving no residue; it dissolves readily in alcohol, but is insoluble in water. The salt is volatile in an atmosphere of steam, and the vapour has a very sweet, camphor-like odour; it is hydrolysed when heated with alcoholic potash for several hours in a reflux apparatus.

Its behaviour towards bromine is somewhat remarkable. Whilst by direct bromination of the original acid only one atom of bromine is introduced into the molecule, the methylic salt is violently acted on by the halogen, and is at once converted into dibromocampholid, a certain quantity of β -monobromocampholid (see below) being produced at the same time.

Anhydride of Camphorenic Acid, $\text{C}_{20}\text{H}_{30}\text{O}_3$.

Phosphorus pentachloride acts readily on camphorenic acid, but on pouring the liquid into cold water, or cold aqueous ammonia, and acidifying the solution, the unaltered substance is precipitated; if,

however, dry ammonium carbonate be substituted for the free alkali, only a portion of the camphorenic acid is recovered unchanged, the remainder being converted into a non-nitrogenous compound having the formula of camphorenic anhydride.

Five grams of the acid was intimately mixed with 7.5 grams of phosphorus pentachloride, this quantity being in slight excess of the amount calculated for one molecular proportion. A violent action took place, and the mixture became liquid; in this condition it was poured on to finely powdered ammonium carbonate, and when the pasty mass at first obtained had become solid, the product was thrown into cold water, in which the greater part dissolved. The insoluble portion was then removed, washed several times with cold water, and recrystallised from alcohol; it separates from concentrated solutions in snow-white plates, and melts at 84–85°.

0.1334 gave 0.3692 CO₂ and 0.1148 H₂O. C = 75.42; H = 9.55.

C₂₀H₃₀O₃ requires C = 75.47; H = 9.43 per cent.

From the above quantity of camphorenic acid, two grams of the anhydride was obtained, rather more than this amount of the unaltered acid being recovered from the alkaline filtrate on acidification.

The anhydride is indifferent towards boiling water, and may be mixed with alcoholic potash without undergoing hydrolysis. It is very readily soluble in organic solvents, and is volatile in an atmosphere of steam.

β-Monobromocampholid, C₁₀H₁₅BrO₂.

Whilst bromination of bromocamphorenic acid gives rise to dibromocampholid, camphorenic acid is converted into a bromolactone isomeric with the monobromocampholid already described as arising from the action of concentrated sulphuric acid on bromocamphorenic acid.

Camphorenic acid is dissolved in cold chloroform, and bromine is added from a burette until the colour of the halogen is no longer destroyed. Before this stage is reached, heat is developed and hydrogen bromide evolved, and, on evaporating the solvent, a pale yellow oil is obtained, which rapidly solidifies to a crystalline cake; this is drained on porous earthenware, crystallised from chloroform, and finally from ether. The substance melts at 62°.

The following results were obtained on analysis.

0.1453 gave 0.2591 CO₂ and 0.0800 H₂O. C = 48.63; H = 6.11.

0.1620 „ 0.1241 AgBr. Br = 32.55.

C₁₀H₁₅BrO₂ requires C = 48.58; H = 6.07; Br = 32.38 per cent.

β-Monobromocampholid is also formed when bromine is added to the dry sodium salt of camphorenic acid. The action is violent,

being accompanied by a hissing noise, and the development of much heat; liberation of hydrogen bromide is, however, not observed. The new isomeride is extremely soluble in organic solvents, and crystallises from ether in hard, transparent prisms; it separates from dilute acetic acid in thin, lustrous plates, and the concentrated solution in alcohol deposits long, striated prisms. The substance is somewhat volatile at 100° , the vapour having a pleasant odour resembling that of α -dibromocamphor; it is volatile in an atmosphere of steam.

Attention has been already drawn to the fact that dibromocampholid is converted into bromocamphorenic acid under the influence of alcoholic ammonia and zinc dust. An analogous change takes place when β -bromocampholid is reduced in this manner, camphorenic acid being formed. The lactone is indifferent towards bromine, and is attacked very slowly by hydrolytic agents.

The specific rotatory power of β -bromocampholid has been the subject of comment in the introductory portion of this paper, it having been observed that the concentration of the solution and the nature of the solvent exert a marked influence on this property. 1.0179 gram dissolved in 25 c.c. of chloroform, at 15° , was found to be inactive, whilst a solution containing 0.7006 gram, in 25 c.c. at the same temperature, gave $\alpha_D = +0^{\circ} 12'$ as the mean of seven concordant readings, whence $[\alpha]_D = +3.5^{\circ}$. A very different result, however, was obtained on using benzene as a solvent, although in the case of this medium concentration has but slight influence on the rotatory power. Thus, a solution containing 0.8810 gram, in 25 c.c. of benzene at 16° , gave $\alpha_D = -1^{\circ} 30'$ as the mean of six concordant readings, corresponding to a specific rotatory power $[\alpha]_D = -21.2^{\circ}$, whilst 1.3711 gram, dissolved in 25 c.c. at the same temperature, gave $\alpha_D = -2^{\circ} 18'$, whence $[\alpha]_D = -21.0^{\circ}$.

Campholid, $C_{10}H_{16}O_2$.

The transformation of bromocamphorenic acid into the isomeric α -bromocampholid finds a parallel in the conversion of camphorenic acid into campholid under the influence of concentrated sulphuric acid. In describing the preparation of camphorenic acid, attention was drawn to the importance of effecting complete reduction of the bromocamphorenic acid, and as an instance of the tenacity with which bromine remains in the product, it may be mentioned that a specimen of campholid, obtained from camphorenic acid containing a small quantity of the halogen, was found to retain an appreciable amount of the impurity after passing successively through the operations entailed in its preparation for analysis, namely, dissolution in sulphuric acid, crystallisation, and sublimation. It is possible, how-

ever, to obtain a pure specimen of campholid by boiling the crude product during several minutes with alcoholic potash, and precipitating the lactone by water.

Camphorenic acid, which has been reduced to powder, is added in small quantities to about five times its bulk of concentrated sulphuric acid; as the substance dissolves, the temperature rises slightly. When clear, the pale yellow solution is poured into a large volume of cold water, and the white, flocculent precipitate is collected, washed several times with cold water, and boiled during a few minutes with alcoholic potash, to which a considerable quantity of cold water is then added. After being washed carefully with cold water, the product is dried on porous earthenware, and crystallised from hot petroleum, separating as the solvent cools in minute, colourless crystals; it melts at $176\text{--}177^\circ$. The following results were obtained on analysis.

0.1020 gave 0.2660 CO_2 and 0.0907 H_2O . $\text{C} = 71.12$; $\text{H} = 9.88$.

$\text{C}_{10}\text{H}_{16}\text{O}_2$ requires $\text{C} = 71.43$; $\text{H} = 9.52$ per cent.

Campholid has the odour of camphor, and closely resembles that substance in appearance, moderate pressure converting it into a translucent mass, which, however, does not exhibit on the surface of water, the gyratory motion peculiar to camphor. It is an extremely volatile substance, and sublimes slowly below 100° ; when heated at the melting point, however, sublimation is extremely rapid, and if the vapour is allowed to cool very slowly, campholid is deposited in beautiful, fern-like aggregates, composed of elongated octohedra. The substance is very volatile in an atmosphere of steam, and the camphor-like odour of the hot vapour is extremely powerful.

Campholid dissolves in most organic solvents with great readiness, and has not as yet been obtained in crystals having well defined geometrical structure; it is less readily soluble in cold petroleum, from which it separates in feathery aggregates when evaporation of the solvent is slow. The lactone is indifferent towards bromine, and is very slowly attacked by hydrolytic agents.

A solution containing 1.0011 gram of campholid in 25 c.c. of chloroform was examined in a 2-decimeter tube at 17° ; the mean of seven concordant observations gave $\alpha_D = +2^\circ 12'$, which corresponds to the specific rotatory power $[\alpha]_D = +27.4^\circ$.

Hydrolysis of Campholid.

At one stage of the investigation, before the lactonic character of campholid was recognised, it was anticipated that the carbonyl group would possess ketonic properties, and an attempt was accordingly made to prepare an oxime; the product, however, consisted of a non-

nitrogenous substance, which evidently arises from addition of the elements of water to the campholid molecule, the action being most likely due to the influence of alcoholic potash.

1.7 gram of the lactone was dissolved in alcohol containing 2 grams of potassium hydroxide; 1 gram of hydroxylamine hydrochloride was then added, and the liquid heated for $1\frac{1}{2}$ hour on the water bath, alcohol being added from time to time. It was then evaporated, the residue being treated with water in order to separate the product from insoluble matter consisting of the unaltered lactone. On reducing the filtered liquid to small bulk, and rendering it acid with concentrated hydrochloric acid, a pale, yellow oil separated, which rapidly became crystalline and hard when rubbed with a glass rod; after being washed and dried, the product was crystallised from hot ethylic acetate, which dissolves it readily, allowing it to separate in magnificent, lustrous needles as the liquid cools. The substance melts to a clear liquid at 179° , and evolves gas at this temperature.

0.1612 gave 0.3798 CO_2 and 0.1376 H_2O . $\text{C} = 64.25$; $\text{H} = 9.48$.

0.1743 „ 0.4090 „ „ 0.1577 „ $\text{C} = 64.00$; $\text{H} = 10.05$.

$\text{C}_{10}\text{H}_{18}\text{O}_3$ requires $\text{C} = 64.51$; $\text{H} = 9.67$ per cent.

The acid dissolves readily in organic solvents, but is only sparingly soluble in water; it dissolves in an aqueous solution of sodium carbonate, and the liquid thus obtained does not decolorise potassium permanganate immediately in the cold.

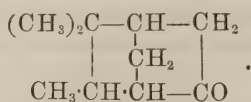
The *barium* salt was prepared by the protracted action of a hot aqueous solution of barium hydroxide on campholid; it separated in white scales on evaporating the solution, and was found on analysis to contain 26.47 per cent. of barium, the percentage required by the formula $(\text{C}_{10}\text{H}_{17}\text{O}_3)_2\text{Ba}$ being 26.00.

Theoretical.

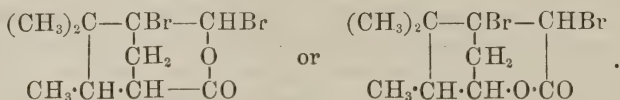
Although our knowledge of the structure of camphor is not sufficiently accurate to render the constitutional expression of the new derivatives a simple exercise, it may not be altogether unprofitable to discuss the relationship which they exhibit among themselves.

It may be safely assumed that the complex $\cdot\text{CHBr}\cdot\text{CO}\cdot$ occurs in bromocamphor, and there appears to be no evidence opposed to the view that the group $\cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CO}\cdot$ is present in α -dibromocamphor; with this provision, the development of a scheme illustrating the mutual connection between these new compounds would present no great difficulty, were it not for the fact that the tendency of recent investigation is to show that the carbonyl group occurs in camphor as the member of a ring containing five carbon atoms. Thus

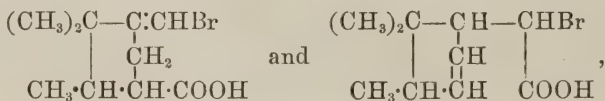
F. Tiemann (*Ber.*, 1895, **28**, 2182) has advanced the conclusion that camphor must be represented constitutionally by the formula



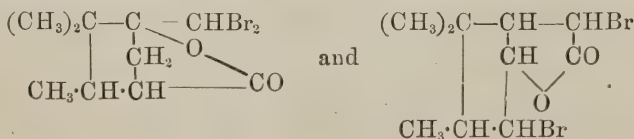
Assuming that α -dibromocamphor contains the group already indicated, this conception demands the representation of dibromocampholid by one of the formulæ



Neither of these expressions, however, is in accordance with the properties of the substance. The bromocarboxylic acids derived from them would be $\gamma\delta$ -acids, having the constitution expressed by the formulæ



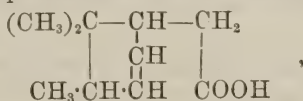
respectively. A systematic study of the properties of $\gamma\delta$ -unsaturated acids as a class has been hitherto impossible, owing to the lack of general methods of preparation. In the aliphatic series, however, allylacetic acid has been obtained, and is found to yield $\gamma\delta$ -dibromovaleric acid on bromination (*Annalen*, 1881, **208**, 100), and γ -bromovaleric acid when combined with hydrogen bromide. The former substance has no tendency to pass spontaneously into a δ -lactone, whilst boiling water converts γ -bromovaleric acid into the lactone of γ -hydroxyvaleric acid. The slight evidence available, therefore, seems opposed to the view that $\gamma\delta$ -unsaturated acids behave in the same way as those containing the ethylenic linking in the $\beta\gamma$ -position, and it is probable that if elimination of hydrogen bromide did follow immediately on the addition of bromine, as is the case with the latter class, the result would be the same as among these acids, so far as the structure of the lactone-ring is concerned, that is to say, γ -lactones would be formed. Assuming this to be the case, bromocamphorenic acid should yield a dibromolactone, having the constitution expressed by one of the following formulæ.



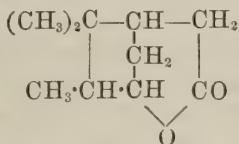
But it has been already stated that dibromocampholid is the product of this change, and if the constitution of that substance is to be represented by the latter scheme, the former being obviously inappropriate, it must be assumed that under the influence of nitric acid, the

ring $\begin{array}{c} \cdot\text{CH}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \text{CH}_2 \text{---} \text{CBr}\cdot \end{array}$ opens, and then re-closes, forming the complex $\begin{array}{c} \cdot\text{CH}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \cdot\text{CHBr}\cdot\text{CH} \text{---} \text{O} \end{array}$, an assumption which seems scarcely tenable.

There is, moreover, another obstacle regarding the constitution of dibromocampholid as represented by the second of the above expressions. Camphorenic acid would have the constitution



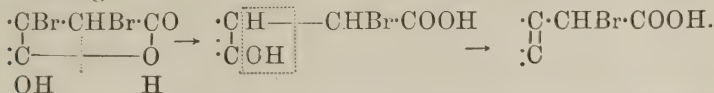
whilst the formula



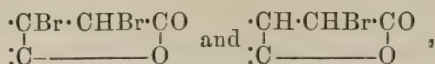
would represent the structure of campholid, and it will be at once noticed that these expressions have been already adopted by Tiemann (*loc. cit.*) in explaining the behaviour of β -campholenic acid and dihydrocampholenolactone, to which camphorenic acid and campholid bear no resemblance, although they are respectively isomeric with these substances.

Whatever conclusion is arrived at regarding the constitution of camphor itself, the relationship between the new derivatives will meet with explanation if the view be taken that dibromocampholid contains

the group $\begin{array}{c} \cdot\text{CBr}\cdot\text{CHBr}\cdot\text{CO} \\ | \quad \quad | \\ \cdot\text{C} \text{---} \text{O} \end{array}$. The changes which result in the production of bromocamphorenic acid from dibromocampholid most probably involve hydrolysis of the lactone ring, substitution of hydrogen for bromine, and elimination of the elements of water, as indicated in the following manner.



The last of these expressions represents the complex occurring in bromocamphorenic acid, and assuming that an acid of this nature would exhibit the behaviour of aliphatic $\beta\gamma$ -unsaturated acids, the action of bromine and sulphuric acid would give rise to compounds containing the groups



peculiar to dibromocampholid and α -monobromocampholid respectively. Under the influence of the same agents, camphorenic acid would yield compounds in which occur the groups



which are most likely present in β -bromocampholid and campholid respectively. The steps by which reduction of the former gives rise to camphorenic acid, would then be parallel with those changes which result in the production of bromocamphorenic acid from dibromocampholid.

It is anticipated that oxidation of the new derivatives will throw light on their constitution, and experiments are being now carried on in this direction.

I cannot conclude this paper without expressing my indebtedness to Professor Armstrong and Dr. Kipping, not only for the interest they have exhibited in the progress of the work, but also for the valuable advice of which I have frequently had the benefit.

Note by Dr. Armstrong.—I desire to take this opportunity of pointing out that the investigation of the derivatives of camphor containing halogens, is at present being pursued in a variety of directions in my laboratory. Although, as Dr. Forster says, there is no evidence opposed to the view that the bromine atoms in α -dibromocamphor are attached to different carbon atoms, and the peculiar readiness with which one is eliminated, lends much support to this view, there are not a few facts which are difficult to reconcile with such a conclusion. Dr. Forster's work—interesting as are the results—has not thrown the light on this question I had anticipated. It is to be expected that the investigation of the nitrocamphor derivatives, and of the derivatives containing two different halogens, as well as the comparison of α - with β -dibromocamphor, will afford evidence of the desired character. The important discovery of a *cis*- and *trans*-nitrobromocamphor made by Drs. Kipping and Lapworth (Proc., No. 157, 209), is of special interest in this connection. I may mention that Dr. Lapworth has proved that when α -dibromocamphor and bromochlorocamphor are sulphonated, the halogen is partially displaced, products different from those investigated by Kipping and Pope being formed. β -Dibromocamphor has also given interesting results.

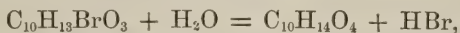
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V.—*w*-Bromocamphoric Acid.

By F. STANLEY KIPPING, Ph.D., D.Sc.

ALTHOUGH the bromocamphoric anhydride, which was first prepared by Wreden a long time ago (*Annalen*, 1872, **163**, 330), has been investigated by several chemists during recent years, the corresponding bromocamphoric acid has not hitherto been isolated. As is well known, the anhydride is slowly decomposed by boiling water, yielding, as principal product, camphanic acid,



the lactone of a hydroxycamphoric acid which, apparently, does not exist, except in the form of a salt. A similar change occurs when bromocamphoric anhydride is boiled with sodium carbonate solution, but, under these conditions, as Aschan has recently pointed out (*Ber.*, 1894, **27**, 2112), a much larger quantity of lauronic acid is formed than is the case when water alone is employed.

The fact that bromocamphoric acid has never been found amongst the various products obtained from the anhydride on treatment with water or alkalis, might be accounted for in one of two ways; it might be, as Aschan assumes (*loc. cit.*), because bromocamphoric acid, like dimethylfumaric acid (pyrocinchonic acid), and diethylfumaric acid (xeronic acid), for example, is actually incapable of existing under ordinary conditions, owing to the readiness with which anhydride formation takes place; or else because the acid loses hydrogen bromide and passes into camphanic acid with extreme facility.

In the course of an investigation of π -bromocamphoric acid (*Proc.*, 1895, 33, 88, and 210), the results of which will form the subject of a future paper, this question of the possible existence of a bromocamphoric acid, corresponding with Wreden's anhydride, came into prominence. π -Bromocamphoric acid, $\text{C}_{10}\text{H}_{15}\text{BrO}_4$, a structural isomeride of the unknown bromo-acid, was found to be stable under ordinary conditions, as was also π -dibromocamphoric acid, $\text{C}_{10}\text{H}_{14}\text{Br}_2\text{O}_4$, a compound in which one of the bromine atoms doubtless occupies the same relative position in the molecule as the halogen atom in Wreden's bromocamphoric anhydride.

These observations seemed to indicate that suitable conditions alone were required for the successful preparation of the bromocamphoric acid in question; this conclusion was ultimately verified by experiment.

On treating Wreden's bromocamphoric anhydride with concentrated nitric acid in the manner described below, it is partially transformed into the corresponding acid of the composition $\text{C}_{10}\text{H}_{15}\text{BrO}_4$;

this acid is a well-defined, crystalline, moderately stable compound, which closely resembles the π -bromo- and π -dibromocamphoric acids in ordinary properties.

As it is convenient to have some means of distinguishing by name the two structurally isomeric monobromocamphoric acids now known, the compound derived from Wreden's anhydride will subsequently be referred to as *w*-bromocamphoric acid; a purely arbitrary designation of this kind (the initial letter of Wreden's name), has, no doubt, its disadvantages, but is probably less misleading than any other.

In a recent paper (*Ber.*, 1894, **27**, 2112), Aschan describes the results of some experiments on *w*-bromocamphoric anhydride; on treating *l*-isocamphoric chloride with bromine, he obtained as principal product *w*-bromocamphoric anhydride, and in one experiment he also succeeded in isolating a very small quantity of a brominated acid, which separated from water in long needles, melting at 196°. Although unable to obtain sufficient for an analysis, he studied the action of sodium carbonate on this brominated acid, and, from its behaviour, concluded that it was probably a bromisocamphoric acid, $C_{10}H_{15}BrO_4$. In the last number of the *Berichte* (*Ber.*, 1895, **28**, Ref., 922), there is an abstract of another paper by the same author, and it is there stated that *l*-bromisocamphoric acid has been isolated from the products obtained on brominating *d*-camphoric acid and *l*-isocamphoric acid; this compound is described as separating from benzene in crystals of the composition $C_{10}H_{15}BrO_4 + \frac{1}{2}C_6H_6$, and melting at 196°. Unfortunately, the original publication (*Acta. soc. scient. fenn.*, **21**, No. 5, 1) is not yet accessible, so that it is impossible, from the data at hand, to say with certainty whether Aschan's acid, which appears to be the same as that mentioned by him in the earlier paper (*loc. cit.*), is identical with, or different from, the *w*-bromocamphoric acid described below. In his interesting paper (*Ber.*, **27**, 2001) on the relation between the various camphoric acids, Aschan himself has shown that the lævorotatory *w*-bromocamphoric anhydride is partially converted into *l*-isocamphoric acid on reduction with zinc dust and acetic acid, from which it would be concluded that simple hydrolysis of the lævorotatory *w*-bromo-anhydride should also afford *l*-bromisocamphoric acid. The properties of Aschan's *l*-bromisocamphoric acid, however, are certainly different from those of the compound obtained by the author; although, apparently, the two substances have practically the same melting point, *w*-bromocamphoric acid is insoluble, or nearly so, in benzene, and cannot be recrystallised from water; at ordinary temperatures it is practically insoluble in this liquid, and, even on boiling, it passes into solution only very slowly, being at the same time decomposed.

Preparation of w-Bromocamphoric Anhydride.—The preparation of the material required for this investigation was very kindly undertaken by Mr. Panisset, a student of the Chemical Department of the Central Technical College, the method adopted having been that described by Reyher (*Inaug. Diss., Leipzig, 1891*), which seemed more convenient than Aschan's process when small quantities only are required.

The bromine having been added gradually to the mixture of pure *d*-camphoric acid and amorphous phosphorus, until the evolution of hydrogen bromide suddenly slackened, the heating on a water bath was continued for a short time, in order to volatilise the excess of halogen; water was then added, in small quantities at a time, cooling well, and later on a little alcohol, in order to dissolve the oil with which the crystals were mixed. The product was then separated by filtration, washed with a little alcohol, dried on porous earthenware, and purified by recrystallisation from chloroform; 8.5 grams of camphoric acid gave 7 grams of crude crystalline product, from which 5.4 grams of pure *w*-bromocamphoric anhydride were obtained; the yield was therefore about 50 per cent. of the theoretical, or much the same result as that obtained by Reyher and Aschan.

w-Bromocamphoric acid.

The pure *w*-bromocamphoric anhydride (m. p. 214°), in quantities of 2—5 grams, was placed in a small, glass, evaporating basin, and rather more than covered with concentrated nitric acid (sp. gr. 1.42); the basin was then covered with a clock-glass and heated on the water bath. The anhydride quickly passed into solution, especially on stirring, and a slight evolution of ruddy fumes was observed, but there was no odour of bromine. As soon as all had dissolved, the clock-glass was removed and the heating continued during two or three minutes longer; the solution was then allowed to cool, diluted with water, and the colourless, crystalline product separated by filtration, washed with water, and placed on porous earthenware. As soon as it appeared to be dry, it was treated with a relatively large quantity of cold chloroform; the greater part, consisting of large crystals of *w*-bromocamphoric anhydride, soon passed into solution, but a small portion of a crystalline powder did not dissolve; this was separated by filtration and washed repeatedly with chloroform, first on the filter and finally on unglazed earthenware.

This product was found to be an acid, and at first it seemed possible that it might be the isocamphanic acid, $C_{10}H_{14}O_4$, described by Reyher (*loc. cit.*), this substance being also practically insoluble in chloroform; as, however, the two compounds differed considerably in melting point, this possibility was excluded.

Camphanic acid, the formation of which under the above conditions was not improbable, is so readily soluble in chloroform that its presence was impossible; the compound obtained in the manner just described was therefore some new derivative of *w*-bromocamphoric anhydride.

As 5 grams of the anhydride had only afforded 0.2 to 0.3 gram of the new acid, a few attempts were now made to improve the method of preparation, but not with any success. On heating the bromo-anhydride with concentrated nitric acid during a longer time than 3—4 minutes, it undergoes oxidation to a greater extent, the yield of the desired product is no larger, and a greater proportion of the anhydride is wasted. The use of a larger quantity of nitric acid, with the object of preventing crystallisation until the solution had cooled to a temperature considerably below 100°, appeared also to give no better results.

The original method was, therefore, again adopted, the anhydride, which was recovered in a practically pure condition on evaporating the chloroform extract of the crude product, being continually used for a following experiment; working in this way, 4.7 grams of the anhydride, after three operations, gave rather more than 0.7 gram of the pure acid, and 3.8 grams of the anhydride were recovered; it is consequently an easy matter to prepare the acid in moderately large quantities.

The crude crystalline acid, freed from anhydride by repeatedly washing with chloroform, was dissolved in dry ether, the filtered solution evaporated to a small bulk, and mixed with a large quantity of chloroform; the crystals which were at once deposited from the hot solution were then separated by filtration, washed with chloroform, and heated for a short time in a water oven.

An analysis of this preparation gave results agreeing well with those required for a bromocamphoric acid.

0.1527 gave 0.2404 CO₂ and 0.0745 H₂O. C = 42.93; H = 5.43.

C₁₀H₁₅BrO₄ requires C = 43.01; H = 5.37 per cent.

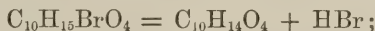
That the substance is a bromocamphoric acid corresponding with Wreden's anhydride is amply proved by the experiments described below.

w-Bromocamphoric acid crystallises from a hot mixture of ether and chloroform in small, transparent prisms or plates, but, when crystallisation takes place slowly at ordinary temperatures, the acid is deposited in large, orthorhombic pyramids; it melts at 195—196°, at the same time effervescing violently and charring slightly. It is practically insoluble in chloroform and in benzene, but it dissolves freely in cold ether, acetone, and alcohol; in these respects, it resembles the π -bromo- and π -dibromo-camphoric acids (Proc., *loc. cit.*).

When a concentrated solution of the acid in sodium carbonate is warmed for a few minutes and then acidified, an oily or crystalline precipitate is produced; this product is formed with elimination of hydrogen bromide, and should, therefore, be ordinary camphanic acid. In order to prove this, some pure *w*-bromocamphoric anhydride was boiled for a short time with sodium carbonate and dilute alcohol, and the camphanic acid thus prepared was compared directly with the compound obtained in a similar way from the *w*-bromocamphoric acid. Both preparations crystallised from dilute alcohol in fern-like prisms, and in long needles, identical in appearance; these crystals in both cases melted in their water of crystallisation when suddenly heated at about 140° ; but after recrystallisation from chloroform, in which they were readily soluble, both specimens melted, although not very sharply, at $198-200^{\circ}$ (pure camphanic acid melts at 201°).

When finely divided *w*-bromocamphoric acid is shaken with a fairly large relative quantity of cold water, it does not dissolve to any appreciable extent, but on boiling it slowly passes into solution; this solution gives a precipitate immediately on the addition of a solution of silver nitrate, but it does not give a crystalline deposit on simply cooling, unless it has been previously concentrated to a very small bulk; the needles which then separate are readily soluble in cold chloroform, and melt at about $198-200^{\circ}$ after recrystallisation.

w-Bromocamphoric acid is, therefore, decomposed by boiling water, giving camphanic acid and hydrogen bromide,



from cold alcohol and acetone, however, it is, apparently, deposited unchanged, as the crystals are insoluble in chloroform; it may also be inferred that the dry acid is stable at temperatures below about 180° , since melting point determinations, under different conditions as to the rate of heating, give concordant results.

A final proof that the compound here described is a bromocamphoric acid, corresponding with Wreden's anhydride, is afforded by its behaviour with acetyl chloride; it dissolves slowly in this liquid in the cold, and seems to be deposited unchanged on evaporating the solution at ordinary temperatures; when, however, the solution is warmed for a short time, the acid is converted into its anhydride. This anhydride is readily soluble in hot chloroform, but only sparingly in ether, and separates from a mixture of these solvents in colourless prisms melting at 214° , and identical in other respects with the crystals of *w*-bromocamphoric anhydride; a mixture of this preparation with some pure *w*-bromo-anhydride melted sharply at 214° .

The above account of the properties of *w*-bromocamphoric acid explains the difficulty met with in its preparation; on the one hand,

the anhydride is not very easily hydrolysed; on the other, the bromo-acid is readily converted into camphanic acid.

During this investigation it has often happened that solutions of *w*-bromocamphoric anhydride in chloroform have been rapidly evaporated on a water bath in order to recover the anhydride; in some cases, but by no means frequently, the solvent may be removed almost entirely before crystallisation commences, and a highly supersaturated solution results; when, finally, crystallisation occurs it is attended with a fairly loud report, and the liquid contents of the vessel are almost instantaneously transformed into a dry, rather bulky, mass of small crystals, free from any visible quantity of liquid chloroform, although still smelling slightly of the solvent.

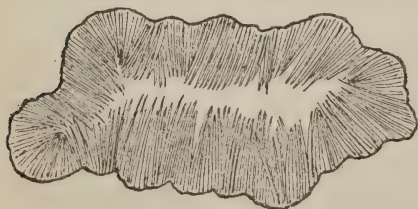
Chemical Research Laboratory,

City and Guilds of London Central Technical College.

VI.—*Efflorescence of Double Ferrous Aluminium Sulphate on Bricks exposed to Sulphur Dioxide.*

By DAVID PATERSON.

It is well known that in certain volcanic districts, such as in Sicily, the neighbourhood of Naples, Iceland, Auvergne, and elsewhere, natural alums are found in the shape of white effloresced salts produced by the action of sulphurous vapours on aluminous minerals such as lava or trachyte. An interesting example of the formation of a similar aluminous salt has been found on the bricks which form the inner wall of wool-bleaching chambers, and which are thus exposed to the sulphur dioxide fumes employed in the bleaching process. After the bleaching chambers have been in use for a year or so, there appears on various parts of the bricks, wherever there are most bases present, a white flocculent covering composed of clusters of glistening crystals, often beautifully and regularly crystallised. When such a cluster is broken up, it exhibits a silken or fibrous mass



Nodule opened, showing crystalline structure.

of white crystals resembling asbestos in texture. This silken appearance of these natural efflorescences has suggested the popular names "hair salt" and "feather alum." Their crystalline structure may be seen from the accompanying drawing taken from a specimen. The

more perfect of these crystals measured from 9 to 10 mm. in length.

In course of time, the bricks exfoliate and become completely disintegrated from the formation of crystals within them. When a brick is thus broken down it is found to be permeated with sulphurous and sulphuric acids, while little tufts of crystals are formed throughout its whole mass. Along with these white crystals, but in very small quantity, is sometimes found a dull, yellowish substance which, on subsequent analysis, was found to contain ferric sulphate. Various specimens of these salts were collected for analysis, and from the results obtained it was found that their composition closely agreed with some of the natural iron alums found in various parts of the world. The following, for instance, is an analysis given many years ago, by Forchhammer, of a natural iron aluminium sulphate in Iceland, and, when compared with the analyses of these salts formed on bricks exposed to sulphur dioxide, it will be seen they are very similarly constituted.

Iceland "Iron Alum" (Forchhammer).

FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	MgO.	H ₂ SO ₄ .	H ₂ O.	Total.
4·57	1·23	11·22	2·19	35·16	45·63	100·00

Samples 1, 2, and 3 were quite white, but 4 was of a dull, yellowish colour owing to the presence of a larger percentage of ferric salt. The results of analysis were as follows:—

Sample.	1.	2.	3.	4.
Ferrous oxide.....	5·53	5·38	5·65	6·20
Ferric oxide.....	0·49	0·98	0·86	2·05
Alumina.....	11·33	9·20	11·45	7·96
Magnesia.....	1·06	0·65	0·82	1·24
Sulphuric acid.....	42·13	40·14	41·09	39·50
Sulphurous acid.....	trace	trace	trace	trace
Water.....	39·46	43·65	40·13	38·49
Silica, lime, brick, sulphur..... } insoluble matter..	—	—	—	4·56
	100·00	100·00	100·00	100·00

The above results show that these salts, from their varying composition, cannot be regarded as definite chemical compounds, as no two analyses agree. If, however, their impurities be not taken into consideration, it will be found they closely resemble, on an average, the formula of a double ferrous aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 + \text{FeSO}_4 + 24\text{Aq}$, as may be seen thus.

	Fe.	Al.	SO ₄ .	H ₂ O.	Impurities.	Total.
Found....	5.61	5.76	43.37	44.31	1.02	100.07
Theoretical	6.04	5.83	41.46	46.67	—	100.0

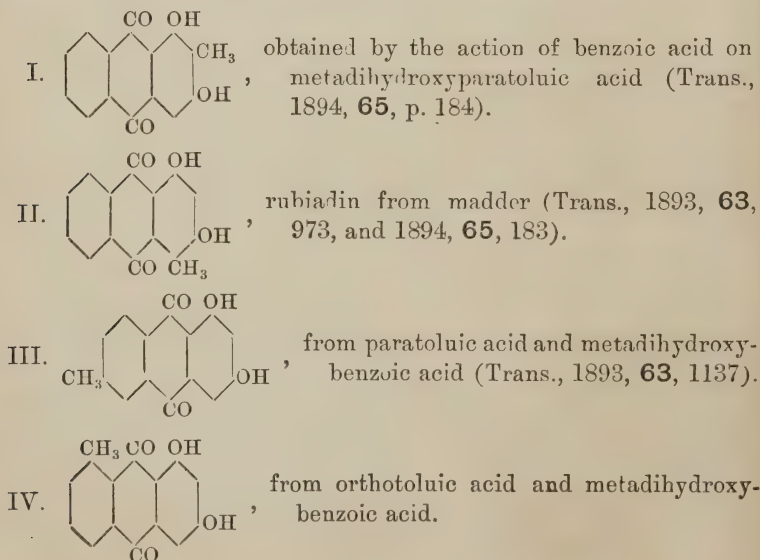
The chemical composition of the clay from which these bricks are made is as follows.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Alkalis.	H ₂ O.	Total.
63.50	14.80	2.05	5.40	6.10	5.50	2.65	100.0

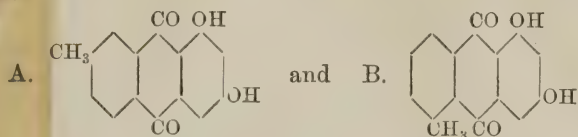
VII.—Some Derivatives of Anthraquinone.

By EDWARD SCHUNCK, Ph.D., F.R.S., and LEON MARCHLEWSKI, Ph.D.

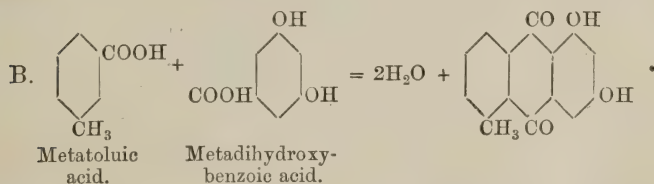
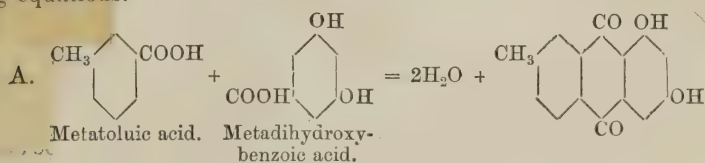
IN our previous communications, we gave a description of three different artificial methylpurpuroxanthins; one of these was obtained by the condensation of paratoluic acid with metadihydroxybenzoic acid and was found by Hummel and Perkin (*Trans.*, 1894, **65**, 854) to be identical with a substance obtained by them from the *Mang-koudu* root. Another one was prepared by the action of benzoic acid on metadihydroxyparatoluic acid; a comparison of this substance with rubiadin enabled us to point out the constitution of the latter. Finally we prepared a fourth methylpurpuroxanthin by the action of orthotoluic acid on metadihydroxybenzoic acid. The constitution of these four substances is represented in the following graphic formulæ



This substance has been prepared by us already a year ago. Up to the present the following two methylpurpuroxanthins were unknown.



It was to be expected that both these substances would be obtainable by the action of metatoluic acid on metadihydroxybenzoic acid, since the former possessing an asymmetrical structure should be able to react with the latter in two different ways, as shown by the following equations.



The process of condensation was brought about in the following way: metadihydroxybenzoic acid (1 part), and metatoluic acid (4 parts), were heated with sulphuric acid (25 parts) for 10 hours at 110°. The dark brown solution containing the above mentioned methylpurpuroxanthins, together with unaltered metadihydroxybenzoic and metatoluic acids as well as anthrachryson, the latter formed by the condensation of two molecules of the dihydroxy-acid, was poured into water and the whole extracted with ether; the ethereal extract was then evaporated and the residue treated with steam in order to expel unaltered metatoluic acid.

The remaining liquid was again evaporated, and by extracting with boiling benzene, the methylpurpuroxanthins were dissolved; the separation of the substances contained in this benzene solution is very difficult since the two methylpurpuroxanthins which are formed, like the methylpurpuroxanthins in general, have very similar properties. Two substances differing from one another in their melting points may however be obtained in the following manner.

The benzene is evaporated and the residue, which melts at about 225—235°, is dissolved in boiling alcohol; to this solution, an equal

volume of benzene is added, and the mixture, if left for some time, deposits orange coloured needles; these are collected and subjected to the same treatment several times, whilst the first filtrate must be evaporated and the residue treated again in a similar manner. Finally two substances with different melting points are obtained, of which the more easily soluble has the lower melting point; but we think that it would be useless to mention their respective melting points, as we were unable to completely separate the two.

(I.) Analysis of the substance with the higher melting point.

(II.) That of the lower melting point.

I. 0.1021 gave 0.2642 CO_2 and 0.0379 H_2O . $\text{C} = 70.66$; $\text{H} = 4.12$.

II. 0.0988 gave 0.2561 CO_2 and 0.0339 H_2O . $\text{C} = 70.60$; $\text{H} = 3.80$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C} = 70.86$; $\text{H} = 3.93$ per cent.

In order to determine the constitution of these two substances, we studied their products of oxidation.

The substance of lower melting point, of which we had a somewhat larger quantity, when mixed with dilute nitric acid (1 : 10) and heated on a water bath, gradually dissolved giving a bright yellow solution, which left a yellowish residue on evaporation. This was redissolved in hot water and lead acetate added; the white precipitate thus produced, being finally decomposed with dilute sulphuric acid, and the mixture extracted with ether. The ethereal solution after evaporation gave nearly white crystals, which on recrystallisation melted at 216° .

The acid was evidently a tricarboxylic derivative of benzene, and, judging by the melting point and its general properties, must have been 1 : 2 : 4-trimellithic acid, $\text{C}_6\text{H}_3(\text{COOH})_3$, and the constitution of the lower melting methylpurpuroxanthin is represented therefore by the formula A (p. 69).

The body with higher melting point, when treated in a similar way, gave a trace of a substance which melted at about 180° , and in all probability was hemimellithic acid, a circumstance which shows that the methylpurpuroxanthin of higher melting point has the constitution represented by formula B.

Methylpurpuroxanthin, $[\text{OH} : \text{OH} : \text{CH}_3 = 1 : 3 : 1']$.

A mixture of 4 grams of dihydroxybenzoic acid, 15 grams of orthotoluic acid, and 200 grams of sulphuric acid was heated for 15 hours at $110\text{--}120^\circ$; the product was then poured into water and extracted with ether; the residue left on evaporating the ethereal extract was suspended in water, and the excess of orthotoluic acid present driven off by means of a current of steam. This was followed by treatment with boiling benzene and the residue was dried in a vacuum.

sited crystalline needles, which, after being recrystallised three times from hot benzene, melted at 246° , and yielded the following results on analysis.

0.1254 gave 0.3249 CO_2 and 0.0484 H_2O . $\text{C} = 70.66$; $\text{H} = 4.29$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C} = 70.86$; $\text{H} = 3.93$ per cent.

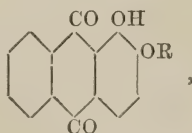
It dissolves in alkalis, forming a red liquid. The solution in concentrated sulphuric acid is brownish-red, and shows a narrow absorption band in the red. The substance is easily soluble in alcohol or ether, and is obtained in orange-coloured, pointed prisms on evaporating the ethereal solution.

Acetyl Derivative of Methylpurpuroxanthin,
 $[\text{OAc} : \text{OAc} : \text{CH}_3 = 1 : 3 : 1']$.

In order to acetylate the above methylpurpuroxanthin, it was digested with acetic anhydride and a small fragment of stannous chloride; the excess of acetic anhydride was then decomposed with alcohol, and, after driving off the ethylic acetate, the residue was crystallised from alcohol. In this way a product was obtained crystallising in lustrous, silky needles, and melting at 195° . It is not changed by cold alkalis, but is decomposed on heating with them.

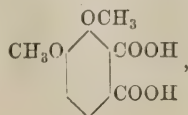
Ethers of Alizarin.

We proposed some time ago the following formula for the monethers of alizarin, obtainable by heating alizarin with caustic potash and an alkylic iodide,



and we pointed out (Trans., 1894, 65, 186) that the natural methyl ether discovered by Hummel and Perkin (Trans., 1893, 63, 1174) in the Chay root contains, probably, the methyl group attached to the oxygen of the α -hydroxy-group. This view has been lately adopted by the above-mentioned chemists (Trans., 1895, 67, 819).

We think that our suggestion finds experimental support in a work of Lagodzinski (*Ber.*, 1895, 23, 1427) lately published. This chemist obtained a monomethyl ether of alizarin by using hemipinic acid,



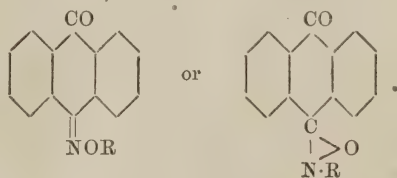
which, considering the kind of reaction adopted, and the properties of the methoxy group adjoining one of the carboxylic groups, must have the same constitution as the ether formed direct by alkylation of alizarin. The properties of both substances agree in every particular, except as regards the melting point. Lagodzinski finds this to be 201° , whilst we determined it as 228° , a new determination giving the same value. This difference might be due to one of the substances being impure; we consider our preparation to be pure.

Ethers of Anthraquinoneoxime.

In a preliminary communication (*Ber.*, 1894, **27**, 2125), we showed that the oxime of anthraquinone can be easily etherified. It suffices to boil an alkaline solution of anthraquinoneoxime with an alkyl iodide; after boiling for two or three hours, the solution is poured into water, the deposit is collected, and washed, firstly, with a weak solution of sodium hydroxide, and finally with water.

We propose here to describe these substances more accurately, but before doing so, some remarks concerning the constitution of these compounds might be of use.

The constitution of the anthraquinoneoxime ethers may be in accordance with either of the two following formulæ,



The first formula would show that these ethers are so called oxygen ethers, whilst the second suggests that they are nitrogen ethers; the method of preparation, however, would in all probability lead to the formation of oxygen ethers, as it is well known that the alkali salts of oximes are generally derivatives of true isonitroso-compounds. Therefore the substitution of the metal by an alkyl group would cause the formation of an oxygen ether. This is supported by the following facts.

If the benzyl ether of anthraquinoneoxime is boiled with strong hydriodic acid, benzylic iodide is formed, and is easily detected by its characteristic odour. Accordingly, if the methyl ether is heated with hydriodic acid in an apparatus similar to Zeisel's, methylic iodide is given off. Were those compounds nitrogen ethers, benzylamine and methylamine respectively would be formed.

Methyl Ether of Anthraquinoneoxime.

This was obtained by the above-mentioned method. The product, after washing with a dilute watery solution of sodium hydroxide, was crystallised from dilute alcohol, the crystallisation being repeated three times. The methyl ether melts at 147° , crystallises in yellowish needles and is easily soluble in organic solvents, especially ether; the latter solution, when treated with hydrogen chloride, did not give any precipitate, and the residue left on evaporation melted at exactly the same temperature as the pure methyl ether. This fact again confirms the above-mentioned formula, as it is known that nitrogen ethers of the oximes under these circumstances give hydrochlorides.

0.2091 gave 0.5836 CO_2 and 0.0899. $\text{C} = 76.12$; $\text{H} = 4.77$.

$\text{C}_{15}\text{H}_{11}\text{NO}_2$ requires $\text{C} = 75.94$; $\text{H} = 4.64$ per cent.

The molecular weight determined in the ethereal solution by means of the ebullioscopic method was found to be normal.

$$k = 2110.$$

0.2290 gave 46.14 Et. $\Delta = 0.045^{\circ}$.

Mol. wt. calculated = 237. Mol. wt. found = 234.

Ethyl Ether of Anthraquinoneoxime.

The oxime was dissolved in absolute alcohol, a few drops of a concentrated solution of potassium hydroxide added, and the mixture boiled for three hours, after adding some ethylic iodide. The solution soon loses its dark brown colour, becoming pale yellow, and if the tint does not change after adding more potassium hydroxide, the treatment may be stopped, and the solution poured into water. The whole is now extracted with ether, and the residue left on distilling off the ether is crystallised three times from dilute alcohol. The ethyl ether melts at a much lower temperature than the methyl ether, namely at 97° .

0.2073 gave 10.99 c.c. of moist nitrogen at 24° and 762 mm. $\text{N} = 5.90$.

$\text{C}_{16}\text{H}_{13}\text{NO}_2$ requires $\text{N} = 5.57$ per cent.

Benzyl Ether of Anthraquinoneoxime.

The alcoholic alkaline solution of the oxime was boiled with the calculated quantity of benzylic chloride, the solution poured into water, and the benzyl ether extracted by agitation with ether; the residue left on evaporating the ether was crystallised from alcohol. If the alcoholic solution is too concentrated, an oil separates, which becomes crystalline after a time; as these crystals are never quite pure, it is advisable to prepare a dilute solution, and induce crystal-

lisation by adding a crystalline fragment of the benzyl ether. The benzyl ether crystallises very well, and is easily soluble in alcohol, ether, benzene, and chloroform. It melts at 82° .

0.1258 gave 0.3709 CO_2 and 0.0569 H_2O . $\text{C} = 80.40$; $\text{H} = 5.01$.

$\text{C}_{21}\text{H}_{15}\text{NO}_2$ requires $\text{C} = 80.51$; $\text{H} = 4.7\%$ per cent.

VIII.—*Researches on the Terpenes. VI. Products of the Oxidation of Camphene; Camphoic acid and its Derivatives.*

By J. E. MARSH and J. A. GARDNER.

IN the Transactions for 1891, p. 64, we describe the method employed for the oxidation of camphene by nitric acid, by which we obtained camphoic acid, a new acid of the formula $\text{C}_{10}\text{H}_{14}\text{O}_6$. In this paper we give an account of some further experiments made with camphoic acid, and describe the isolation of other acids formed along with it by the oxidation of camphene; we also make some general observations as to the chemical nature of camphene, and its relationship to the terpenes, to camphor, and to camphoic acid.

Camphoic acid.

This acid was obtained in the way already described by heating camphene with nitric acid of sp. gr. 1.3 on the water bath; the crude acid is best purified by crystallisation from hot nitric acid of sp. gr. 1.42, in which it is readily soluble, crystallising out almost completely on cooling. The melting point was wrongly given at $184\text{--}185^{\circ}$ in the former paper; we find, however, that the acid melts at a temperature approaching 200° , whether crystallised from ether, from nitric acid, or from water, but the melting point is not quite exact as the substance begins to decompose before it melts; thus a specimen of the acid crystallised from ether melted at $197\text{--}198^{\circ}$, whilst another specimen twice crystallised from nitric acid melted at 196° , and after two further crystallisations from water it still melted at 196° , in each case decomposing at the same time. The specimen of highest melting point was that obtained from anhydrocamphoic acid, a compound described in this paper; prepared in this way, it melts and decomposes at $199\text{--}200^{\circ}$.

A specimen of the acid obtained from anhydrocamphoic acid gave on analysis

	Found.	Calculated for $\text{C}_{10}\text{H}_{14}\text{O}_6$.
Carbon.....	51.97	52.1 per cent.
Hydrogen	6.19	6.0 ,,

Camphoic acid was also obtained by the oxidation of chloro-camphenephosphoric acid, $C_{10}H_{14}Cl \cdot PO_3H_2$, by means of nitric acid. This acid is produced by the action of phosphorus pentachloride on camphene and subsequent treatment of the product with water; it was treated with nitric acid in the same way as described for camphene. The camphoic acid obtained from it was crystallised from ether and analysed. It gave

	Found.	Calculated for $C_{10}H_{14}O_6$.
Carbon.....	52.23	52.17 per cent.
Hydrogen.....	6.39	6.08 „

This acid also split up on distillation into carbon dioxide, and camphopyric anhydride.

Camphoic acid has a sharp, acid taste, and is very soluble in water, alcohol, and ether, but less so in benzene or petroleum. It is a tribasic acid, and forms salts with one, two, or three molecular proportions of base. A crystalline barium salt of the formula $BaC_{10}H_{12}O_6$ was described in the former paper; it had an acid reaction. Most of the salts of camphoic acid are soluble in water, but the copper and lead salts are almost insoluble. The sodium salt was not prepared, but on mixing weighed quantities of camphoic acid with two and three equivalents of caustic soda we found that the disodic camphoate is acid while the trisodic camphoate is alkaline.

The triammonium camphoate is prepared by dissolving dry camphoic acid in dry ether and passing in dry gaseous ammonia. The precipitated salt must be collected rapidly and placed in a dry atmosphere over sulphuric acid, as it is deliquescent and turns yellow on exposure to moist air. It is obtained in this way as a white, friable mass, melting at $198-199^\circ$ and at the same time decomposing. A determination of nitrogen gave

	Found.	Calculated for $C_{10}H_{11}O_6(NH_4)_3$.	Calculated for $C_{10}H_{12}O_6(NH_4)_2$.
N	13.51	14.94	10.6 per cent.

This salt is very soluble in water, and on evaporating the solution, ammonia is evolved and the monoammonium salt formed; this separates in white, glistening crystals, which melt at $208-210^\circ$, and at the same time decompose.

A determination of nitrogen gave the following result.

	Found.	Calculated for $C_{10}H_{13}O_6 \cdot NH_4$.
N	5.86	5.67 per cent.

The copper salt is obtained by boiling a solution of sodium camphoate with copper sulphate, when it separates as a pinkish precipitate, which redissolves on cooling the solution. The triplumbic

camphoate is obtained as a white precipitate on adding lead acetate or lead chloride to a solution of sodium camphoate. The precipitate when dried at 100° gave on analysis

	Found.	Calculated for $\text{Pb}_3(\text{C}_{10}\text{H}_{11}\text{O}_6)_2$.
Lead.....	56.5	57.7 per cent.

A specimen dried at 120° gave lead 58.5.

Anhydrocamphoic acid, $\text{C}_{10}\text{H}_{12}\text{O}_5$.

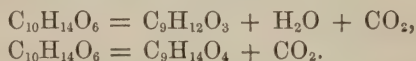
This acid is obtained by the action of acetyl chloride on camphoic acid. When camphoic acid is heated with acetyl chloride, it slowly dissolves with evolution of hydrogen chloride; the solution is then evaporated to dryness, and the residue crystallised from ether. It crystallises in large, transparent plates from ether or ethylic acetate, melting and decomposing at 205°. Its formula, $\text{C}_{10}\text{H}_{12}\text{O}_5$, is that of camphoic acid less H_2O . On analysis it gave

	Found.	Calculated for $\text{C}_{10}\text{H}_{12}\text{O}_5$.
Carbon.....	56.51	56.6 per cent.
Hydrogen	5.93	5.6 „

Anhydrocamphoic acid has a sweet taste very different from the sharp acid taste of camphoic acid. It is only slightly soluble in benzene, chloroform, petroleum, or cold water; it is readily soluble in hot water, and on cooling crystallises out in part unchanged; part, however, is hydrolysed. It crystallises best from dry ether or from ethylic acetate, and is precipitated from its solution in ether on the addition of light petroleum. It dissolves in sodium carbonate, and is precipitated unchanged by the addition of hydrochloric acid.

When anhydrocamphoic acid is boiled with water preferably containing a little acid, it is gradually hydrolysed with production of camphoic acid. The camphoic acid obtained in this way melts at 199–200° with decomposition. The analysis of it is given on page 74.

It was stated in the former paper that when camphoic acid is distilled it undergoes decomposition yielding carbon dioxide, water, camphopyric anhydride, and isocamphopyric acid.



When anhydrocamphoic acid is heated above its melting point, it decomposes into camphopyric anhydride and carbon dioxide.



The reaction appears to be quantitative, but it is difficult to obtain an exact result owing to the sublimation of the camphopyric an-

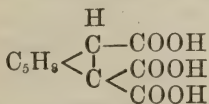
hydride. A weighed quantity of anhydrocamphoic acid was heated in a tube connected with a drying tube and potash bulbs; the tube was heated in a sulphuric acid bath above the melting point of the substance until the effervescence ceased, and the decomposition appeared to be complete; a current of air was then drawn through the apparatus. The experiment gave

	Found.	Calculated.
Total loss of weight of anhydrocamphoic acid	20	20 per cent.
Gain of weight of drying tube...	1	0 „
Gain of weight of potash bulbs (carbon dioxide)	17	20 „

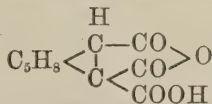
The loss of weight in excess of the amount of carbonic acid appeared to be due to sublimation of the anhydride, some of which may have found its way into the drying tube.

Anhydrocamphoic acid is a monobasic acid, neutralising one equivalent of caustic soda; but the point of neutralisation is difficult to hit, owing to the rapid hydrolysis of the anhydride by the action of caustic soda, the colour produced on the indicator, phenolphthaleïn, rapidly disappearing as the soda is taken up.

The relation subsisting between camphoic acid and anhydrocamphoic would be that represented by the formulæ



Camphoic acid.



Anhydrocamphoic acid.

Camphopyric acid, cis-.

When camphoic acid is distilled, camphopyric anhydride, $\text{C}_9\text{H}_{12}\text{O}_3$, is obtained; this, when dissolved in hot caustic soda, is converted into camphopyric acid, $\text{C}_9\text{H}_{14}\text{O}_4$. Camphopyric anhydride is also obtained by heating anhydrocamphoic acid above its melting point; further, if camphoic acid is heated above its melting point, it undergoes decomposition, with loss of carbonic acid, but without appreciable loss of water if the temperature be not allowed to rise much above the melting point of the substance. In this way, the acid is produced directly from camphoic acid, the reaction taking place thus: $\text{C}_{10}\text{H}_{14}\text{O}_6 = \text{CO}_2 + \text{C}_9\text{H}_{14}\text{O}_4$. The product thus obtained dissolved almost entirely in cold solution of sodium carbonate, and the precipitate produced by hydrochloric acid after two crystallisations from water melted at $203\text{--}204^\circ$. It contains some mesocamphopyric acid, a substance to be mentioned later (p. 79).

Camphopyric acid is a dibasic acid, and requires two molecular

proportions of sodium hydroxide for neutralisation. 0.186 gram acid required 10 c.c. of standard sodium hydrate (1 c.c. = 0.008 NaHO) for neutralisation (calculated for dibasic acid 10 c.c.). It closely resembles camphoric acid as to the solubility of its salts, they being in general soluble in water, but the lead and copper salts, like those of camphoric acid, are insoluble in water, and are precipitated on adding a soluble lead or copper salt to a solution of the sodium salt of the acid. The lead salt thus obtained as a white precipitate was analysed after being dried at 110°. It gave

	Found.	Calculated.
Lead	52.5	52.9 per cent.

The sodium salt was prepared and analysed; it is extremely soluble in water, and, on evaporating, the solution is left in a syrupy condition, but it can be crystallised from a mixture of ether and alcohol. After drying at 120°, it gave

	Found.	Calculated.
Sodium	19.57	20.00 per cent.

Camphopyric Anhydride, cis-.

This compound, described in a former paper, is formed by distilling camphoric acid, by heating anhydrocamphoric acid above its melting point, and also by the action of acetyl chloride on *cis*-camphopyric acid; the yield in the last case is over 90 per cent. It is also formed by the action of water on camphopyryl chloride. The analogy between camphopyric acid and camphoric acid is also borne out by the nature and modes of production of their anhydrides. The two anhydrides are very similar in appearance and in properties; they are both very stable with regard to the action of water; they may both be crystallised from water unchanged; they are both volatile at 100°, and may be sublimed at this temperature, and they are both volatile in steam. In one point, however, they differ, the melting point of camphoric anhydride being higher, whilst that of camphopyric acid is lower than the melting points of their respective acids.

Camphopyric acid, m. p. 209°. Camphoric acid, m. p. 185°.
Camphopyric anhydride, m. p. 178°. Camphoric anhydride, m. p. 220°.

Camphopyryl chloride, $C_{10}H_{12}O_2Cl_2$.—When camphopyric acid is treated with phosphorus pentachloride, it gives the acid chloride $C_{10}H_{12}O_2Cl_2$; this is best obtained by mixing camphopyric acid with a slight excess of the pentachloride in a mortar, the acid being added gradually, and the whole well stirred; in this way, the formation of anhydride is avoided. The oxychloride of phosphorus is then dis-

tilled off under ordinary pressure, and the camphopyryl chloride under diminished pressure; it comes over at 125—130° under 13 mm. pressure. The above method is also satisfactory in the preparation of camphoryl chloride from camphoric acid.

Camphopyryl chloride is a colourless liquid, resembling camphoryl chloride in smell, reacting slowly in cold water, but readily soluble in and hydrolysed by hot water; it is only slowly acted on by sodium hydrate solution when cold. The amount of sodium hydrate required to neutralise the acids formed on hydrolysis of camphopyryl chloride was determined by dissolving the chloride in standard sodium hydroxide in excess, the excess of sodium hydrate being determined by standard nitric acid. It was found that one molecular proportion of camphopyryl chloride required 3.86 (theory 4.0) molecular proportions of sodium hydroxide. The chlorine was also determined by titration with standard silver nitrate solution, using potassium chromate as indicator.

	Found.	Calculated.
Chlorine	31.1	31.8 per cent.

Action of Water on Camphopyryl Chloride.—It was found by Marsh (*Proc. Roy. Soc.*, 1890, **47**, 6) that when the acid chloride of ordinary dextrocamphoric acid was treated with boiling water, it was converted into a mixture of the anhydride of dextrocamphoric acid and a new camphoric acid which was found to be lævorotatory. This acid was readily separated from the anhydride of the dextro-acid, with which it was mixed, by treatment with a cold solution of sodium carbonate.

The relationship of these two camphoric acids to one another led Marsh to consider one of them, namely, the dextrorotatory, as the *cis*-, and the lævorotatory as the *trans*-modification, corresponding to Baeyer's *cis*- and *trans*-hydroterephthalic acids. Shortly before the publication of Marsh's paper, Professor Friedel had announced the discovery of the same lævocamphoric acid which he had obtained from the long known mesocamphoric acid. It then appeared that mesocamphoric acid was nothing else but a mixture of the dextro- and lævo-camphoric acids.

Mesocamphopyric acid.

When camphopyryl chloride is treated with boiling water, it does not behave quite in the same way as camphoryl chloride, but the whole of the chloride readily goes into solution, and is hydrolysed; the acid was obtained from this solution, the yield being theoretical. It was found to be quite different from the original camphopyric acid, and subsequent examination proved it to be a mixture of the original acid, which we call the *cis*-modification, with a new isomeric

acid, *trans*-camphopyric acid. This mixture of acids we call *meso*-camphopyric acid to recall its analogy to mesocamphoric acid. The mesocamphopyric acid crystallises well from water, having all the appearance of a single substance; its melting point, however, is not quite constant, varying between 160° and 170° . This acid appears to be identical with the acid which we formerly described as isocamphopyric acid produced along with camphopyric anhydride by the distillation of camphoic acid; it is also produced when camphoic acid is heated just above its melting point, in which case there is excess of the ordinary *cis*-camphopyric acid produced.

Camphopyric acid, trans-.

Mesocamphopyric acid, when treated with acetyl chloride, is separated into its constituents, the *cis*-acid being converted into anhydride, while the *trans*-acid is left unaltered, and the two can then be separated by the action of a solution of sodium carbonate, which dissolves the *trans*-acid and leaves the *cis*-anhydride unaltered. The acid so obtained, after a second treatment with acetyl chloride, was crystallised from water. It melted at 190 — 191° . It was analysed and gave

	Found.	Calculated for $C_9H_{14}O_4$.
Carbon	57.7	58.0 per cent.
Hydrogen	7.7	7.5 „

A better way to obtain the *trans*-camphopyric acid is to leave camphopyryl chloride exposed to moist air for some hours. In this way the liquid becomes converted into a dry, white, crystalline mass consisting of a mixture of the *trans*-acid with the anhydride of the *cis*-acid. The two are then separated by treatment with a solution of sodium carbonate. On precipitating the sodium carbonate solution by hydrochloric acid and crystallising from water, the acid is obtained melting at 191° .

The *meso*-acid was prepared synthetically by mixing equal weights of the *cis*- and *trans*-acids, and crystallising from water; it is obtained thus as a homogeneous, crystalline substance, melting between 163° and 170° . The melting points of the three camphopyric acids are thus closely analogous to those of the three corresponding camphoric acids, the *trans*-acid in each case melting at a lower temperature than the *cis*-, and the *meso*-acid lower than either of its constituents.

Chlorocamphopyryl Chloride.

In preparing camphopyryl chloride by the action of phosphorus pentachloride on camphopyric acid, we found that if the pentachlo-

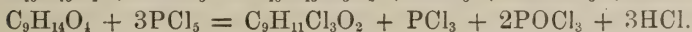
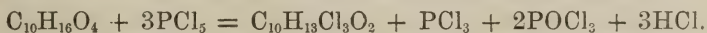
ride is in excess and the mixture is heated on the water bath, the acid chloride produced contains more chlorine than is required by the formula $C_9H_7O_2Cl_2$; thus a specimen prepared in this way and distilled under diminished pressure at $132-133^\circ$ was analysed, the chlorine being estimated by Carius' method. It gave

	Found.	Calculated for $C_9H_7O_2Cl_2$.
Chlorine	32.9	31.8 per cent.
„	33.1	— „

It was suspected that, by the action of heat on the camphopyryl chloride in presence of excess of pentachloride of phosphorus, chlorine is substituted for hydrogen, as was found by Marsh to occur in the case of camphoric acid under similar circumstances (*Proc. Roy. Soc., loc. cit.*). Accordingly camphopyric acid was treated in order to produce chlorocamphopyryl chloride in the same way as camphoric acid was treated to produce chlorocamphoryl chloride. Eight grams of camphopyric acid were heated with 33 grams of phosphorus pentachloride in a flask on a sand bath, the flask being provided with a reflux condenser; hydrogen chloride was evolved, and the product became liquid. After about seven hours' heating, the evolution of hydrogen chloride had practically ceased, and, on cooling, the liquid was poured off from the excess of pentachloride, which had crystallised out. It was distilled at first under ordinary pressure, when it began to boil at 85° , the temperature rising slowly, showing the presence of phosphorus trichloride along with the oxychloride. The substance was then distilled under 15 mm. pressure, when it boiled at 142° . It is a colourless liquid. The chlorine was determined.

	Found.	Calculated for $C_9H_{11}O_2Cl_3$.
Chlorine	41.7	41.3 per cent.

It thus appears that camphopyric acid undergoes the same reaction as camphoric acid, as expressed by the following equations.



Chlorocamphoryl Chloride.

As the notice in the Proceedings of the Royal Society with regard to this substance was very brief, it may not be out of place here to give some further details about it.

Camphoric acid, mixed with about $4\frac{1}{2}$ times its weight of phosphorus pentachloride, was heated in a flask provided with a reflux condenser on a sand bath for 17 hours; the trichloride and oxychloride of phosphorus were then distilled off under ordinary pressure,

and the residue fractionally distilled under diminished pressure. After three distillations, a liquid was obtained boiling at 145–148° under pressure (11 mm.), which solidified on cooling. The chlorine was determined in this specimen.

	Found.	Calculated. $C_{16}H_{13}Cl_3O_2$.
Chlorine	39.37	39.23 per cent.
„	39.27	— „

The amount of the pure substance so obtained was 70 grams from 100 grams of camphoric acid, 40 grams of less pure substance being also obtained. Chlorocamphoryl chloride is a nearly colourless, crystalline solid, melting when the flask containing it is held in the hand at a temperature of about 28°.

Chlorocamphoric Anhydride.

When chlorocamphoryl chloride is poured into seven or eight times its weight of boiling water, it remains at the bottom of the vessel in the form of an oil, which gradually becomes solid; the solid was washed with sodium carbonate solution, in which very little dissolved, and, as it gave off hydrogen chloride on drying, it was again treated with hot water, then washed with sodium carbonate, and dried. From 70 grams of chlorocamphoryl chloride, 50 grams of chlorocamphoric anhydride were thus obtained, or over 90 per cent. of the theoretical yield. The substance, crystallised from benzene, melted at 233–234°; another specimen melted at 235°. The chlorine was estimated.

	Found.	Calculated. $C_{10}H_{13}ClO_3$.
Chlorine	16.22	16.39 per cent.

If chlorocamphoryl chloride is boiled with water until it is entirely dissolved, camphanic acid is obtained on concentrating the solution; it separates at first as an oil, which crystallises after a time.

The crystals effloresce in the desiccator. I, a portion was dried at 100° and analysed; II is another specimen prepared in the same way.

	Found.		Calculated. $C_{10}H_{14}O_4$.
	I.	II.	
Carbon	60.25	60.51	60.60 per cent.
Hydrogen	7.07	7.27	7.07 „

The barium salt gave 25.4 per cent. Ba, found.

„ „ 25.8 „ „ calculated.

The salt is completely soluble in water and on slow evaporation gives crystals.

Aschan has recently described the production of chlorocamphoric anhydride in another way, and has shown that it is converted into camphanic acid by boiling with caustic soda. We may be permitted to say that our work above described on chlorocamphoric chloride, chlorocamphoric anhydride and camphanic acid, was done during or before the year 1889.

Chlorocamphopyric Anhydride.

Chlorocamphopyryl chloride is only very slowly acted on by water; if, however, it is dissolved in ether and this solution is allowed to remain in contact with water, large, colourless crystals gradually form between the ethereal and aqueous layers. These crystals are nearly insoluble in light petroleum or benzene, more soluble in ether and still more so in chloroform. They melt at 228—229° and gave the following results on analysis.

	Found.	Calculated. $C_9H_{11}ClO_3$.
Carbon	53.04	53.33 per cent.
Hydrogen	5.80	5.44 „
Chlorine	17.50	17.50 „

The substance is chlorocamphopyric anhydride analogous to chlorocamphoric anhydride. We have not yet obtained sufficient of the substance to determine whether an acid analogous to camphanic acid is produced from it, but we have evidence that the acid obtained by dissolving chlorocamphopyryl chloride in sodium hydroxide is not a monobasic lactonic acid like camphanic acid, but a dibasic hydroxy-acid. This point, however, we must reserve, and we hope to make it the subject of a future communication to the Society.

Camphopyranilic acid.

Camphopyric acid forms an anilic acid, again closely analogous to the anilic acid from camphoric acid. Camphopyric anhydride was heated with aniline and the melt, which became solid on cooling, after being washed with dilute hydrochloric acid to free it from aniline, was crystallised from alcohol. Camphopyranilic acid is then obtained in colourless crystals, melting at 212°, of the formula $C_9H_{12} < \begin{smallmatrix} CO \cdot NH \cdot C_6H_5 \\ COOH \end{smallmatrix}$. It is soluble in soda and reprecipitated by hydrochloric acid.

	Found.	Calculated.
Carbon	68.84	68.96 per cent.
Hydrogen	7.39	7.23 „
Nitrogen	5.41	5.36 „

Action of Hydrogen Iodide on Camphopyric acid.

Sixteen grams of camphopyric acid were heated with 32 c.c. of hydriodic acid of sp. gr. 1·8, and a little red phosphorus in sealed tubes; the action is very slow, the tubes containing some crystalline matter after prolonged heating. They were heated in all for 40 hours at first at 220°, and finally to 280°; the contents of the tubes were then liquid. The liquid was made alkaline with soda and distilled in steam, when a pale yellow, volatile oil came over, this was separated, dried with calcium chloride, and distilled from sodium, when most of it came over at 105—125°. On redistilling this fraction, it boiled at 105—115°; the amount was 2 c.c. On analysis it gave

	Found.	Calculated. C_8H_{16} .
Carbon	85·75	85·71 per cent.
Hydrogen	13·84	14·24 „

By analysis alone it is not possible to distinguish between hexahydro-xylene, C_8H_{16} , and hexahydrotoluene, C_7H_{14} , or any other hydrocarbon of the series. The vapour density, however, showed that the substance was hexahydro-xylene.

Weight of substance taken	0·0891 gram.
Volume of air	18·75 c.c.
Barometer, 761 mm. Temperature, 13° C.	
Hence density ($H = 1$)	56·3.
Density of hexahydro-xylene (calculated)....	56
„ hexahydrotoluene („)....	49

The substance was also nitrated; for this purpose $1\frac{1}{2}$ c.c. of the hexahydro-xylene was heated with 25 c.c. of a mixture of 2 parts of strong sulphuric acid and 1 part of nitric acid. As nothing separated on cooling, the mixture was poured into water, when, on standing, fine crystalline needles were deposited; these, after being washed with water and crystallised from alcohol, melted at 178°, and were evidently trinitrometaxylene. Hence the reduction of camphopyric acid by hydrogen iodide yields hexahydrometaxylene.

Further Products of the Oxidation of Camphene.

Among the other products of the oxidation of camphene by nitric acid, we obtained terephthalic acid, camphoric acid, and succinic acid, besides other substances, the nature of which we have not yet determined.

After camphoric acid has been separated from the crude product of oxidation, a syrupy mass is left; most of this dissolves on treating it with ether, leaving terephthalic acid as an insoluble white

powder. This was converted into its dimethylic salt by treatment with phosphorus pentachloride and methylic alcohol. On crystallising the product from methylic alcohol, it melted at 140—141°.

When the ethereal solution of the syrupy mass was shaken up with sodium carbonate solution, a considerable amount was left dissolved in the ether, having apparently no acid properties, and on separating the ethereal solution, a yellow oily residue was left. On attempting to distil this yellow oil, it suddenly and violently decomposed, after removal of the flame, evolving gas and leaving a small quantity only of carbonaceous residue in the flask.

The sodium carbonate solutions were acidified, but no definite substance could be obtained from them; on distilling the product which separated, however, a large quantity of camphopyric anhydride was obtained, hence the oily matter probably still contained camphoric acid. Besides the camphopyric anhydride, an oil was obtained on distillation; this was volatile in steam, lighter than water, and had a camphorous smell. It was shaken out with ether and distilled. It boiled at about 250°, and gave on analysis

	Found.	Calculated, $C_8H_{12}O_2$.
Carbon	68·46	68·57 per cent.
Hydrogen	8·78	8·57 „

It appears to be saturated as it does not take up bromine. One gram was heated at 100° with baryta water, and the barium salt obtained was converted into the sodium salt by means of sodium carbonate; the sodium salt, after having been freed from carbonate by solution in alcohol, was analysed.

	Found.	Calculated, $C_8H_{13}NaO_3$.
Sodium	13·0	12·7 per cent.

The oil thus appears to be a lactone, but it was not obtained in sufficient quantity to enable us to examine it further.

The presence of succinic acid was suspected, by its characteristic taste, in the crude crystals obtained from the mother liquors after separation of the camphoric acid. It was isolated by suitable means, and, after crystallising from water, it melted at 186°. It gave a barium salt insoluble in ammonia; this was analysed.

	Found.	Calculated.
Barium	53·67	54·15 per cent.

Camphoric acid was obtained in small quantity from the crude crystalline camphoric acid by treatment with acetyl chloride, and separated as anhydride from the anhydrocamphoric acid by sublimation at 100° or by treatment with water. After being purified by recrystallisation from boiling water, it was obtained sometimes in

small needles, sometimes in thin leaf-like crystals. The specimens from different samples of camphoric acid, varied somewhat in melting point; one, prepared by sublimation melted at 204° , another, after recrystallisation from water, at $220\text{--}221^{\circ}$, and another at $215\text{--}216^{\circ}$. Another specimen, obtained by treatment with water, melted at $204\text{--}205^{\circ}$ after recrystallisation from absolute alcohol.

Several of these different samples were analysed.

	Found.			Calculated for $C_{10}H_{14}O_3$.
	I.	II.	III.	
C	65.05	65.48	65.35	65.93
H	8.00	7.9	7.75	7.69

Another sample, melting at $215\text{--}216^{\circ}$, was boiled for a long time with water, in which it gradually became more soluble; after being allowed to remain for a long time, it was concentrated to a small bulk, when white, glistening, crystalline leaves separated. These crystals had an acid reaction and melted at $182\text{--}186^{\circ}$. A small portion, on treatment with acetyl chloride, gave an anhydride melting at 213° . The acid was analysed, with the following results.

	Found.	Calculated for $C_{10}H_{16}O_4$.
C	59.71	60.0 per cent.
H	8.29	8.0 ,,

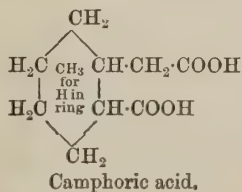
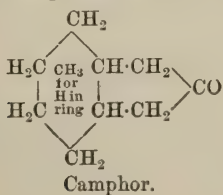
From this it appears that the product of oxidation of camphene contains a camphoric acid, but whether a new one or one already known it is impossible to say, as the quantity was insufficient to determine its optical rotation or to purify it further.

Theoretical Considerations.

The hydrocarbon camphene, from which camphor, camphoric acid, and camphoic acid are derived, is a very stable substance, differing in that respect from the turpentine and citrenes. It appears to be a saturated hydrocarbon, to contain no double linkings, whereas turpentine appears to have one, and citrene two double linkings. Wallach has shown that camphene does not form an additive compound with bromine, but a substituted compound, and our own work on the phosphonic and chlorophosphonic derivatives of camphene shows that the hydrocarbon readily forms substituted, but not additive compounds. Camphene, it is true, forms an additive compound with hydrogen chloride, and this circumstance appears to have led chemists to ascribe a double linking to camphene. But hydrogen chloride and the halogen acids are not, like bromine, reagents specially characterised by their capability of saturating a double linking, although in certain cases they may do so. Hydrogen chloride does not, for example, under ordinary circumstances, if at all,

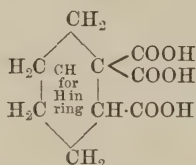
saturate the double linking in ethylene or in allyl alcohol. Now, if camphene contain no double linking, it must be constituted of at least three closed rings, for a compound having ten carbon atoms derived from a fully saturated open chain formula $C_{10}H_{22}$ must, if it remain saturated, close a chain for every pair of hydrogen atoms it loses. If, then, camphene, $C_{10}H_{16}$, is a saturated hydrocarbon constituted of three closed rings, in order to form camphene hydrochloride, $C_{10}H_{17}Cl$, or camphor, $C_{10}H_{16}O$, from it, one of the three closed rings must be broken, leaving two, and to form camphoric acid, $C_{10}H_{16}O_4$ or camphoic acid, $C_{10}H_{14}O_6$, two of the closed rings must be broken, leaving only one. Hence when hydrogen chloride acts on camphene we regard the union of the two, not as the saturating of a double linking, but as the breaking of a ring formation. This is by no means an uncommon action of a halogen acid. Indeed the halogen acids are characterised by their power of breaking feebly united ring structures much more so than is bromine. For example, Freund found that the trimethylene ring is readily broken by hydrogen iodide, but with great difficulty by bromine. Perkin also found that trimethylenedicarboxylic acid was not acted on by bromine at the ordinary temperature, while substitution took place on warming; on the other hand, the ring is immediately broken by hydrobromic acid. Similar instances might be given in the case of other rings.

If, then, camphene may be regarded as constituted of several ring formations, we have next to consider the evidence as to the particular nature of these rings. The production of camphoic acid from camphene, together with its relationship to camphoric acid and to hexamethylene, appears to throw light on this question. The close analogy of camphopyric acid to camphoric acid, and the production of hexahydrometaxylene from each of them, warrants us in assuming that both acids, and also camphoic acid, are substituted derivatives of hexamethylene. Now, since camphoic acid is not formed from camphor or from camphoric acid, it would appear that the camphene molecule is broken down in two ways: (1) to yield camphor and camphoric acid, (2) to yield camphoic acid, in both cases leaving a hexamethylene nucleus untouched. The formulæ given by Marsh (*Proc. Roy. Soc.*, 1890, 47, 6) for camphor and camphoric acid represented them, if we disregard for the moment the position of the methyl group, as follows—

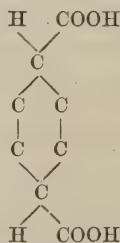


with a methyl group substituted for hydrogen in the hexamethylene ring.

The most probable view of the constitution of camphoic acid appears to us to represent it as a hexamethylene ring with two carboxyl groups replacing hydrogen attached to the same carbon atom, and one carboxyl group replacing hydrogen attached to an adjacent carbon atom, with methyl replacing hydrogen in the ring, thus:

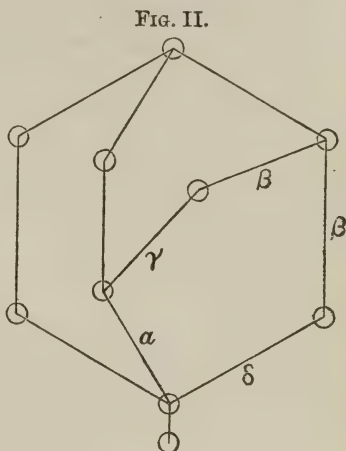
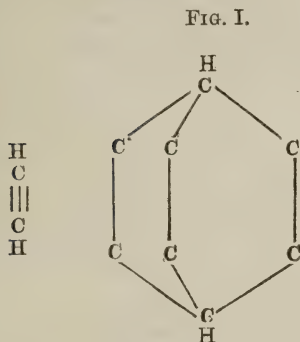


In order to derive the foregoing formulæ for camphor and for camphoic acid from camphene, we have to explain the six carbon and five carbon rings of camphor and the six carbon ring of camphoic acid, which it appears to us is necessarily different from the six carbon ring in camphor and in camphoric acid. We have, then, in camphene a pentamethylene ring and two different hexamethylene rings. These we cannot express by the ordinary cyclic formulæ. We have to give to camphene a tridimensional formula, a formula in which the atoms are not regarded as situated in a plane, but on the surface of a sphere. Such formulæ, which can only be imperfectly represented on paper, may be called *spheric* formulæ to distinguish them from *cyclic* formulæ. They may be regarded as derived from triply-linked carbon atoms in the same way that Baeyer has represented cyclic formulæ as derived from doubly-linked carbon. Baeyer has derived cyclic formulæ from doubly-linked carbon atoms, regarding the carbon atoms as not directly doubly linked, but indirectly through the intervention of other carbon atoms, as, for example, in his comparison of the hexahydroterephthalic acids with maleïc and fumaric acids—



In a similar manner we may regard spheric formulæ as derived from triply-linked carbon atoms, the carbon atoms not being directly

linked by three bonds, but indirectly by the intervention of other carbon atoms, thus (Fig. I) :



a formula made up of three hexamethylene rings.

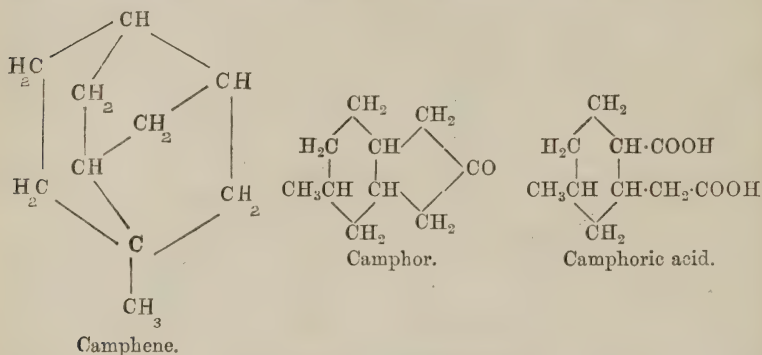
The formula we propose for camphene is derived from this triple hexamethylene spheric formula, thus (Fig. II).

By breaking the link marked α , we derive the formula of camphor; whereas by breaking the two links marked β , and leaving the link α , we derive camphoric acid. In the first case, a pentamethylene and a hexamethylene ring are left, while when the links $\beta\beta$ are broken, a hexamethylene ring only is left, which is, moreover, different from the hexamethylene ring of camphor.

Further, we represent turpentine or pinene by the same structure as camphene, omitting the link γ , and introducing one double linking. The production of camphene from turpentine hydrochloride is readily explained by this hypothesis, which, we believe to be borne out by other reactions of turpentine and its oxidation products. The universally-accepted structure for citrene and cymene is also readily derived from that of turpentine by eliminating the linking δ , and from camphene by elimination of both γ and δ links. The camphor and camphoric acid formulæ, derived from the above camphene formula, differ from those proposed by Marsh in 1889 only in the position of the methyl group in the ring. Against those formulæ, no serious objection has been brought forward except that they do not account for the production from camphoric acid of trimethylsuccinic acid. But the formation of trimethylsuccinic acid appears to us to indicate such a complete breaking down of the camphoric acid molecule, that it would not seem likely to have any more value for the determination of the formula of that compound than, for example,

the formation of methylsuccinic acid from tartaric acid or of alcohol from sugar has for determining the constitution of tartaric acid or of sugar respectively.

The formula now proposed for camphor and camphoric acid, differing, as we have said, from the earlier ones only in the position of the methyl group, are represented below as derived from camphene.



In conclusion, we believe that the formulæ suggested in this paper account in a simple manner for the principal facts relating to the terpene and camphor groups. They account—

1. For the conversion of turpentine, citrene, and camphor into cymene.
2. For the conversion of camphor into carvacrol.
3. For the conversion of turpentine into camphene and into citrene.
4. For the oxidation of camphene to camphor and to camphoric acid.
5. For the absence of double linkings in camphene, and for the presence of one double linking in turpentine and two in citrene.
6. For the production from camphoric acid of camphanic acid, and campholactone.
7. For the relationship of camphoric acid and camphoric acid to hexahydroisoxylene.
8. For the general analogy of camphoric acid and camphopyric acid, and for the stereoisomerism manifested by them.

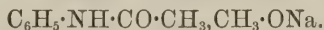
*University Laboratory,
Oxford.*

IX.—*The Action of Sodium Alcoholate on Amides.*

By JULIUS B. COHEN, Ph.D., and WILLIAM H. ARCHDEACON, B.Sc., The Yorkshire College.

AT the meeting of the British Association in 1894 (*Brit. Assoc. Reports*, p. 625) a communication was read by one of us on the constitution of the amides, containing a brief reference to the action of sodium methoxide on acetanilide. As this action appeared to us to have an important bearing on the constitution of the amides, we have studied it more fully, and now bring before the Society the results which we have obtained.

If, to a solution of acetanilide in dry ether, powdered sodium methoxide is added in molecular proportion, it dissolves; but after the lapse of a few minutes, a voluminous crystalline compound is deposited, filling the liquid. This substance has the formula

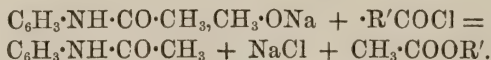


Similar compounds have been prepared with ortho- and para-acetotoluidide and α - and β -acetonaphthalide on the one hand and with sodium methoxide and ethoxide on the other. Benzanilide and form-anilide form similar compounds. With formylphenylhydrazide, however, no additive compounds are formed; but the sodium appears to displace the hydrogen in the amido-groups. In the case of benzamide, a fine granular compound is obtained, which appears to be a mixture of the alcoholate additive compound with sodium benzamide. With propionanilide, butyranilide, diphenylacetamide, and ethylacetanilide no definite compounds have so far been obtained by this method. In the case of propionanilide and butyranilide such compounds appear to exist in solution; for if a little ether be added to either of these substances, sufficient to dissolve a fraction of the whole, the addition of the sodium alcoholate will at once produce a clear solution; on evaporating the ether under diminished pressure, nothing separates out until the greater portion of the ether has gone, when crystals of the unchanged anilide are deposited.

Acetanilide Sodium Methyloxide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3, \text{CH}_3\cdot\text{ONa}$.—1.35 grams of acetanilide is dissolved in dry ether (complete solution is not necessary) and 0.54 gram of finely powdered sodium methoxide is added; on shaking, a clear solution is obtained, but very soon a pasty magma of needle-shaped crystals forms. The crystals are collected, washed with ether, and dried over sulphuric acid in a vacuum. The substance forms a white, apparently amorphous mass. It gave the following results on analysis.

- I. 0.2455 gave 0.0942 Na_2SO_4 . $\text{Na} = 12.47$.
 II. 0.4359 „ 0.1695 „ „ $\text{Na} = 12.59$.
 III. 0.2620 „ 16.1 c.c. dry nitrogen at 13° and 770 mm. $\text{N} = 7.45$.
 IV. 0.1890 „ 0.372 CO_2 and 0.1115 H_2O . $\text{C} = 56.98$; $\text{H} = 6.55$.
 $\text{C}_9\text{H}_{12}\text{NaNO}_2$ requires $\text{Na} = 12.17$; $\text{N} = 7.40$; $\text{C} = 57.14$; $\text{H} = 6.35$.

In some of the subsequent determinations, the sodium has been estimated by decomposing the compound with water and titrating with decinormal oxalic acid, using phenolphthaleïn as indicator. The above compound is quickly decomposed by water and alcohol and also by boiling ether and acetone, which dissolve out the acetanilide. It is also decomposed by acid chlorides, forming the methylic salt of the acid, sodium chloride, and acetanilide according to the equation



If acetyl chloride is added to the calculated quantity of the substance suspended in ether, methylic acetate, sodium chloride, and acetanilide are formed; the latter was identified by decomposing it, with potash, into acetic acid and aniline, and by a nitrogen estimation.

0.1905 gave 17.5 c.c. moist nitrogen at 752 mm. and 16° . $\text{N} = 10.48$.

$\text{C}_8\text{H}_9\text{NO}$ requires $\text{N} = 10.37$ per cent.

Benzoyl chloride acts similarly. From 2 grams of the sodium methoxide compound and 1.79 gram of benzoyl chloride, 1 gram of methylic benzoate, and 1.29 gram of acetanilide were obtained. On heating the compound in a stream of dry hydrogen for four hours to 100° , methylic alcohol distils together with a little aniline; the aniline was identified by converting it into the platinochloride and analysing it.

0.294 gave 0.0955 Pt. $\text{Pt} = 32.48$.

$(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2, \text{H}_2\text{PtCl}_6$ requires $\text{Pt} = 32.66$ per cent.

The residue consisted for the most part of sodium acetanilide.

0.231 gave 15 c.c. moist nitrogen at 759 mm. and 13° . $\text{N} = 7.65$.

$\text{C}_9\text{H}_{12}\text{NNaO}$ requires $\text{N} = 7.40$ per cent.

Further, the sodium acetanilide obtained in this way was treated with benzoyl chloride, when benzanilide, melting at 160° , is formed. The substance was analysed with the following result.

0.1745 gave 11.3 c.c. moist nitrogen at 21° and 760 mm. $\text{N} = 7.38$.

$\text{C}_{13}\text{H}_{11}\text{NO}$ requires $\text{N} = 7.11$ per cent.

The action of iodine on the sodium methoxide compound suspended in ether gives rise to a number of products, among which phenyl-carbamine, acetanilide, and iodoform were identified. Ethylic iodide yields ethyl methyl ether and acetanilide.

The following compounds have been prepared in a manner similar to acetanilide sodium methoxide. Where the amide is but slightly soluble in ether, the sodium alcoholate has been added to the substance suspended in the ether, well shaken, and then filtered or decanted. The clear filtrate, on standing, deposits crystals of the new compound.

Acetanilide sodium ethoxide, $C_6H_5 \cdot NH \cdot CO \cdot CH_3 \cdot C_2H_5 \cdot ONa$.—The preparation of this compound is identical with that of the sodium methoxide compound, and the substance is not distinguishable from the latter.

The following results were obtained on analysis.

0.283 required 13.9 c.c. decinormal oxalic acid. Na = 11.3 per cent.

0.2345 „ 11.7 „ „ Na = 11.4 „

$C_{10}H_{14}NO_2Na$ requires Na = 11.6 per cent.

Paracetotoluidide sodium methoxide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \cdot CH_3 \cdot ONa$.

Prepared as above from paracetotoluidide, gave on analysis.

0.113 required 5.65 c.c. oxalic acid. Na = 11.74 per cent.

$C_{10}H_{14}NO_2Na$ requires Na = 11.33 per cent.

Orthoacetotoluidide sodium methoxide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \cdot CH_3 \cdot ONa$.

0.1705 required 7.8 c.c. oxalic acid. Na = 10.52 per cent.

$C_{10}H_{14}NO_2Na$ requires Na = 11.33 per cent.

α -Acetonaphthalide sodium methoxide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH_3 \cdot CH_3 \cdot ONa$.

This substance crystallises in brilliant, needle-shaped crystals.

0.2875 required 11.6 c.c. oxalic acid. Na 9.3 per cent.

$C_{13}H_{14}NO_2Na$ requires Na = 9.6 per cent.

Paracetotoluidide sodium ethoxide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \cdot C_2H_5 \cdot ONa$

0.176 gave 0.0566 Na_2SO_4 . Na = 10.4 per cent.

0.1413 required 6.5 c.c. oxalic acid. Na = 10.6 per cent.

$C_{11}H_{16}NO_2Na$ requires Na = 10.6 per cent.

Orthoacetotoluidide sodium ethoxide, $CH_3 \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3 \cdot C_2H_5 \cdot ONa$.

0.1335 gave 0.0440 Na_2SO_4 . Na = 10.6 per cent.

$C_{11}H_{16}NO_2Na$ requires Na = 10.6 per cent.

α -Acetonaphthalide sodium ethoxide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH_3 \cdot C_2H_5 \cdot ONa$.

0.4035 required 15.8 c.c. of oxalic acid. Na = 9.0 per cent.

$C_{14}H_{16}NO_2Na$ requires Na = 9.1 per cent.

β -Acetonaphthalide sodium ethoxide, $C_{10}H_7 \cdot NH \cdot CO \cdot CH_3 \cdot C_2H_5 \cdot ONa$.

0.346 gave 0.1 Na_2SO_4 . Na = 9.3 per cent.

$C_{14}H_{16}NO_2Na$ requires Na = 9.1 per cent.

Benzanilide sodium ethoxide, $C_6H_5 \cdot NH \cdot CO \cdot C_6H_5, C_2H_5 \cdot ONa$.

0.3040 required 12.1 c.c. oxalic acid. Na = 9.1 per cent.

$C_{15}H_{15}NO_2Na$ requires Na = 8.7 per cent.

Formanilide sodium methoxide, $(C_6H_5 \cdot NH \cdot COH)_2, C_2H_5 \cdot ONa$.—If sodium methoxide in molecular proportion is added to formanilide dissolved in ether, crystalline nodules of the new compound are deposited on the sides of the flask and the contents eventually become nearly solid. The same thing occurs with sodium ethoxide.

The following are the results of two analyses of the sodium ethoxide compound.

0.398 required 13.1 c.c. oxalic acid. Na = 7.8 per cent.

0.296 " 9.6 " " N = 7.5 "

$C_6H_5 \cdot NH \cdot COH, C_2H_5 \cdot ONa$ requires Na = 12.2 per cent.

$(C_6H_5 \cdot NH \cdot COH)_2, C_2H_5ONa$ " Na = 7.4 "

From this it would appear that in the case of formanilide, 2 mols. combine with 1 mol. of the alcoholate. This might take place in the

following way,

$$\begin{array}{c} C_6H_5 \cdot NNa \cdot CH \cdot OH \\ | \\ C_6H_5 \cdot N \cdot CH(OH) \cdot OC_2H_5 \end{array}$$

Action of Sodium Ethoxide on Benzamide.

In this case, a fine granular precipitate is obtained, which apparently has a constant composition, but this does not correspond with that of any definite compound. It might be a mixture of equal quantities of the additive compound and sodium benzamide. The action is evidently of a different order from that previously described.

Three different preparations gave the following results.

I. 0.196 required 12 c.c. oxalic acid; Na = 14.1 per cent.

II. 0.1785 " 11.1 c.c. " Na = 14.3 "

III. 0.1945 " 12 " " Na = 14.2 "

$C_6H_5 \cdot CO \cdot NH_2, C_2H_5 \cdot ONa$ requires Na = 12.1 per cent.

$C_6H_5 \cdot CO \cdot NHNa$ requires Na = 16.1 per cent.

Action of Sodium Ethoxide and Sodium Methoxide on Diphenylacetamide.

Diphenylacetamide dissolves readily in ether, but on the addition of the alcoholate very little of the latter appears to pass into solution; the clear filtrate gives only a slight, flocculent deposit on standing, and on evaporation in a vacuum, unchanged diphenylacetamide separates.

Action of Sodium Ethoxide and Methoxide on Ethylacetanilide.

The same result was obtained as in the case of diphenylacetamide. On the addition of sodium methoxide to the ethereal solution of the amide, none of the alcoholate appeared to dissolve. Sodium ethoxide was rather more soluble; but in neither case did the ethereal solution, on standing or on evaporation, give any indication of a crystalline additive compound.

Action of Sodium Ethoxide on Formylphenylhydrazide.

On adding sodium ethoxide to formylphenylhydrazide a yellow solution is obtained, from which an orange-yellow compound is deposited; in the dry state this is of a light ochre colour.

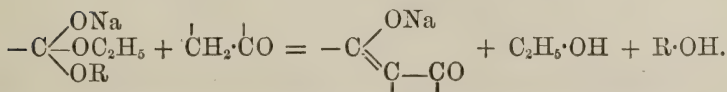
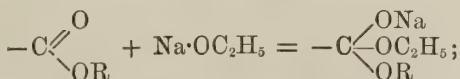
0.0788 gave 0.0623 of Na_2SO_4 ; $\text{Na} = 25.6$ per cent.

$\text{C}_7\text{H}_6\text{N}_2\text{ONa}_2 = 25.5$ per cent.

Apparently, this substance has the formula $\text{C}_6\text{H}_5\cdot\text{NNa}\cdot\text{NNa}\cdot\text{COH}$.

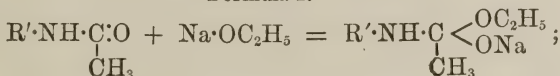
The formation of additive compounds of the acetyl derivatives of aniline, the toluidines, and naphthylamines with sodium methoxide and ethoxide would indicate the presence of an unsaturated group in these amides.

Claisen has shown that such additive compounds are formed in the case of the ethereal salts, and that numerous condensations of these salts with compounds containing the group $\text{CH}_2\cdot\text{CO}$ occur in this manner according to the following equations.

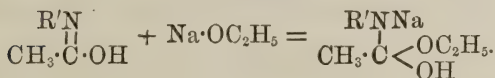


Applying this idea to the acetyl derivatives we may have the addition of the sodium alcoholate taking place in one of the following ways.

Formula I.



Formula II.



The second formula is the one which appears to us to agree best with the properties of the substance. We have shown that alcohol is given off from the additive compound of acetanilide with sodium methoxide on heating, and that sodium acetanilide is formed.

This reaction is confirmed by the experiments of Seifert (*Ber.*, 1885, 18, 1358), who prepared sodium acetanilide by evaporating to dryness an alcoholic solution of sodium ethoxide and acetanilide. Moreover, there is no doubt, considering the formation of alkyl-anilides by the action of alkylic iodides on sodium acetanilide, that the sodium atom is attached to the nitrogen atom. The formation of this sodium compound from acetanilide, sodium methoxide, by heating it, would be difficult to explain by the first formula. This being the case, it would appear probable that acetanilide itself has the formula $C_6H_5 \cdot N \cdot C(OH) \cdot CH_3$.

The fact that diphenylacetamide and ethylacetanilide do not appear to form analogous compounds is then easily explained, for these two compounds contain no replaceable hydrogen, and cannot therefore form a hydroxyl group.

We do not, of course, lose sight of the possibility of a tautomeric change taking place at the moment of formation of these addition compounds, for, as Claisen has pointed out, questions of tautomerism cannot be satisfactorily decided where chemical changes are involved. An attempt to solve the problem by the electrical conductivity of the acid amides, kindly undertaken for us by Dr. Ewan, is described by him in another communication.

X.—*Note on the Electrolytic Conductivity of Formanilide and Thioformanilide.*

By THOMAS EWAN, B.Sc., Ph.D.

It was thought possible that the electrolytic conductivity of the aqueous solutions of the amides might throw some light on their structure; and at Dr. Cohen's request I examined some of them from this point of view. The majority, however, are too sparingly soluble in water to allow of measurements being made, whilst others are decomposed by the water too rapidly. The following numbers were obtained with formanilide. The measurements were made at 25° , and as rapidly as possible, as the conductivity increased on standing. μ is the molecular conductivity in reciprocal Siemen's units, μ_1 and μ_2 refer to two different samples of formanilide which were examined.

$$k = \frac{(\mu/\mu_\infty)^2}{(1 - \mu/\mu_\infty)v}.$$

Concentration (litres containing 1 gram mol.) <i>v</i> .	μ_1 .	μ_2 .	Mean μ .	$k \times 10^{10}$.
10	0.026	0.027	0.0265	5.6
20	0.031	0.034	0.0325	4.2
40	0.040	0.046	0.0430	3.7
80	0.058	0.068	0.0630	3.9
160	—	0.101	0.101	5.1

$\mu_\infty = 355$ (approximately).

A comparison of the value of k above found with its value for acetic acid (180000×10^{-10}) shows that formanilide possesses only extremely feeble acid properties, and it is not surprising that its sodium salt is, as is shown by the following experiment, decomposed in aqueous solution almost completely into caustic soda and formanilide.

2 c.c. water and 20 c.c. N/100 NaOH solution were mixed; conductivity of the mixture = 0.0169.

2 c.c. N/10 formanilide solution and 20 c.c. N/100 NaOH mixed; conductivity of the mixture = 0.0167.

A considerable decrease in the conductivity would have occurred if any appreciable quantity of salt had been formed.

Thioformanilide, $C_6H_5 \cdot NH \cdot CSH$, is very slightly soluble in water (the strongest solution obtainable was N/400), and it decomposes rather rapidly into phenylcarbamine and sulphuretted hydrogen. Its sodium salt appears to exist in aqueous solution.

0.0685 gram of thioformanilide was dissolved in 4 c.c. of 51N/100 NaOH, and the solution made up to 102 c.c. (= N/50). The molecular conductivity of this solution was 180.0 at 25° ; the molecular conductivity of N/50 NaOH at $25^\circ = 217.8$. The quantity of thioformanilide taken was equivalent to one quarter of the caustic soda, so that, assuming that the whole of the thioformanilide was converted into sodium salt, and that both it and the caustic soda are completely dissociated in N/50 solution, the conductivity of the solution may be calculated as follows.

$$\begin{aligned}\mu &= \mu_{Na} + \frac{3}{4}\mu_{OH} + \frac{1}{4}\mu_{(C_6H_5NS)} \\ &= 49 + \frac{3}{4} \cdot 170 + \frac{1}{4} \cdot 35 = 185.\end{aligned}$$

The salt decomposes in the same way as the free thioformanilide.

XI.—*On certain Phenylthiocarbamates.*

By H. LLOYD SNAPE, D.Sc., Ph.D.

IN a paper (Trans., 1885, **47**, 778) published in this Journal some years ago, I described the action of phenylic cyanate on phenylic mercaptan, a phenylic salt of phenylthiocarbamic acid, having the formula $C_6H_5 \cdot S \cdot CO \cdot NH \cdot C_6H_5$ being formed; and I pointed out that an isomeride in which the oxygen and sulphur atoms had exchanged positions might be expected to be obtained by the action of phenylthiocarbimide on phenol. That experiment, and also the action of the same thiocarbimide on phenols, I had proposed to investigate, but, unfortunately, it has been impossible for me to do this until recently. Meanwhile, the reaction with phenol itself has been investigated by Professor A. E. Dixon (Trans., 1890, **57**, 268); but, as this had escaped my attention until my experiments had been completed, and I had obtained a purer product and a better yield, a few notes on my own examination of this reaction may be advantageously added.

Phenylthiocarbimide and Phenol.

These two substances were heated, in molecular proportion, in a sealed tube at temperatures varying from 100° to 280° , and for periods varying from 2 to 67 hours; contrary to Dixon's experience, I found that the higher the temperature, provided it was not allowed to rise much above 270° , and the longer the time during which these substances were heated together, the better was the yield of the thiocarbamate; the temperature should not be allowed to rise above 280° , as decomposition then sets in, and the product is a nearly black mass, from which it is difficult to separate the required crystals.

I obtained the best yield after heating the mixture for nearly three days, the temperature for the greater part of the time varying from 250° to 280° . The product, a viscous, brown liquid, when allowed to stand in the cold, gradually deposited crystals, until, in from three to four days, the whole appeared to have become solid. The yield, under the above circumstances, after washing, pressing, and drying (as described by Dixon), amounted to nearly 25 per cent. of the theoretical; Dixon, working at a lower temperature and heating for a shorter time, obtained only 7 per cent. These crystals were nearly pure, and were readily obtained in perfectly pure condition by crystallisation from absolute alcohol, as well formed, highly lustrous, pale yellow leaves or needles, which melted sharply at 148° (Dixon found the melting point to be between 149° and 151°). The substance

could also be crystallised from glacial or diluted acetic acid, but was insoluble in ether and light petroleum.

A determination of sulphur, by Carius' method, gave the following result.

0.126 yielded 0.129 BaSO_4 . $\text{S} = 14.03$ (Dixon found 13.48).

$\text{C}_{13}\text{H}_{11}\text{NSO}$ requires $\text{S} = 13.97$ per cent.

The other properties described by Dixon for the phenyl salt of ψ -phenylthiocarbamic acid were confirmed.

So much difficulty having been experienced in effecting combination between phenylthiocarbimide and phenol, it was to be anticipated that an action between the former substance and more complex phenols would not readily occur, and, actually, I found it impossible to effect a combination between the above-named thiocarbimide and either resorcinol or quinol. I also tried the effect of heating phenylthiocarbimide with glycol, but again without effecting direct combination. The experiments are briefly summarised below.

Phenylthiocarbimide and Resorcinol.

These two substances were heated together in a sealed tube, in the proportion of twice the molecular weight of the former to once that of the latter; after two hours at 100° to 150° , no change was observable, and, even after heating for another hour at 180° , the resorcinol crystallised out on cooling, and the thiocarbimide had acquired a slightly darker colour. On heating for a further period of $2\frac{1}{2}$ hours at 175 – 180° , a beautiful, blood-red liquid was obtained, from which crystals of resorcinol separated on cooling; the red oil smelt strongly of the thiocarbimide, did not solidify on further cooling, was insoluble in water, readily dissolved in alcohol, glacial acetic acid, and benzene, but at once separated again as an oil on evaporating these solutions.

The oil appeared to be the product of a partial decomposition of the thiocarbimide, and I could not find any trace of the formation of a thiocarbamate.

Phenylthiocarbimide and Quinol.

The results obtained on examining the behaviour of this pair of substances, when heated together, were similar; up to 180° , very little change was observed. After heating for 15 hours at 200° , crystals of quinol separated unaltered, but the thiocarbimide had again sustained some decomposition, the colour having distinctly deepened, and at 220° a black mass was obtained, but no thiocarbamate. I next endeavoured to effect a reaction between these two substances by heating them together first in benzene solution and then in glacial acetic acid solution. The decomposition of the thio-

carbimide, as was to be anticipated, did not take place at as low a temperature as before, but again there was no indication of combination occurring between the two substances.

Phenylthiocarbimide and Glycol.

On heating these two substances together for four hours at 265° , a few minute crystals separated, but I could not succeed in obtaining a sufficient quantity for examination, and longer heating only resulted in effecting decomposition, the entire liquid acquiring a deep, brownish-black colour. From this oil I failed to isolate any crystallisable substance; it dissolved in alcohol, ether, glacial acetic acid, and benzene, but, on evaporating these solutions, only oily drops, consisting of the original materials employed, together with decomposition products, were obtained.

Having thus failed to effect combination between phenylthiocarbimide and dihydroxy-compounds, I next endeavoured to prepare the isomerides of the thiocarbamates I had hoped in this way to obtain, by the action of phenylic cyanate on the corresponding thiophenols, and I completely succeeded, both in the case of dithioresorcinol and of dithioquinol.

These thiophenols I prepared by the method described by Koerner and Monselise (*Gazzetta*, 1876, **6**, 133—142), and found no difficulty in obtaining them in a state of purity, possessing the exact melting points given in the paper by the above-named chemists. In the necessary previous preparation of the respective calcium salts of meta- and para-benzenedisulphonic acids, I noted, however, an error in *Watts's Dictionary* (**1**, 458), which may possibly mislead others. It is there stated that, in separating these calcium salts by crystallisation, the meta-salt separates *first*, whereas the reverse is the case. I was unable to refer to the original papers, and, though it seemed unlikely that only the calcium salt of the meta-acid should be less soluble than that of the para-acid, I was only able to determine this with certainty by the later preparation of the sulphonic chlorides.

Metaphenylene Phenylthiocarbamate.

Phenylic cyanate and dithioresorcinol, in the theoretical proportions, were heated in a sealed tube by means of a water bath containing a solution of common salt; after about half an hour, crystals commenced to separate, and, a few minutes later, the whole solidified to a crystalline mass. This was washed with cold absolute alcohol, to remove any excess of phenylic cyanate, the crystals themselves being almost insoluble in this solvent; they were also insoluble in water, but were dissolved by ether and also by glacial acetic acid, and could readily be recrystallised from these liquids. From glacial

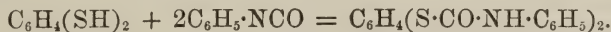
acetic acid, the thiocarbamate separated in the largest crystals, these consisting of white needles, as much as 1 cm. in length, which gradually grew in the solution in beautiful tufts. They melted at 178—179°, and below that temperature were stable; at a higher temperature, however, the substance decomposed with energetic evolution of hydrogen sulphide and other gases possessing an unpleasant odour; but the sulphur was not removed by merely heating some of the crystals in a test-tube with an alkaline solution of lead hydroxide. On heating the crystals with fuming nitric acid, a very fine, wine-red solution was obtained.

An estimation of sulphur, by Carius' method, gave the following result.

0.112 gave 0.138 BaSO₄. S = 16.92.

C₂₀H₁₆N₂O₂S₂ requires S = 16.84 per cent.

The reaction which had occurred is therefore represented by the equation



Paraphenylene Phenylthiocarbamate.

Phenylic cyanate and dithioquinol likewise readily enter into combination, even at the temperature of a water bath. It is not even necessary that they should be heated in a sealed tube, but it is better to do so, if only to protect the phenylic cyanate from the air, and thus to prevent the formation of carbanilide. The crystals formed were at first pale yellow, but, after repeated recrystallisation from boiling acetic acid, they were obtained as small, pure white needles; the individual form of these was scarcely observable by the naked eye, but they tended to group themselves in tree-like aggregates. They were soluble also in ether, but in neither solvent was this substance so soluble as the meta-isomeride, nor did it yield large crystals so readily; it was insoluble in water, and scarcely soluble in cold alcohol, but dissolved in boiling aniline. The crystals melted at 200—202°. The behaviour of the substance when heated to a higher temperature, and also on heating with nitric acid and with an alkaline solution of lead hydroxide, respectively, was similar to that of the meta-compound.

A determination of sulphur, by Carius' method, gave the following result.

0.1 gave 0.123 BaSO₄. S = 16.89 per cent.,

which closely corresponds to the percentage (see preceding) theoretically required.

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XII.—*Periodides of Theobromine.*

By GEORGE ELLIOTT SHAW.

APPARENTLY the only periodide of theobromine hitherto known is that described by Jörgensen (*Ber.*, 1869, **2**, 463), who prepared it by mixing a solution of theobromine in strong hydrochloric acid with potassium iodide and allowing it to stand. It crystallises in nearly black prisms, having the formula $(C_7H_8N_4O_2, HI)_2, I_6$. When attempting to prepare the compound by this method, however, it was found that the nature of the product depended on the relative quantities of hydrochloric and hydriodic acids present; moreover, it is preferable to add hydriodic acid rather than to use potassium iodide, so as to avoid the crystallisation of potassium chloride. With hydrochloric acid in large excess, thin plates were obtained, nearly black by reflected light, but pale brown by transmitted light, and giving a red powder. They contained chlorine as well as iodine. Analyses were made of two different crystallisations.

I. 0.3288 gave 0.3600 AgI + AgCl. 0.3505 of this gave 0.2369 AgCl.

Corresponding to I = 45.00 and Cl = 6.51.

II. 0.1808 gave 0.1994 AgI + AgCl. 0.1860 of this gave 0.1259 AgCl.

Corresponding to I = 44.87 and Cl = 6.73.

These numbers agree with the formula $(3C_7H_8N_4O_2, 2HCl, HI)_2, I_6$.

		Found.	
	Calculated.	I.	II.
I	45.18	45.00	44.87 per cent.
Cl	6.32	6.51	6.73 ,,

With a smaller proportion of hydrochloric acid, another compound is obtained in rhomboidal prisms, nearly opaque and black, but transmitting a little ruby light. It also gives a red powder.

0.3342 required 8.53 c.c. N/10Na₂S₂O₃ solution, equivalent to 32.30 per cent. "exterior iodine," using this term, as applied by Tilden, for the loosely combined iodine.

The analytical results correspond with the formula



		Found.	
	Calculated.	I.	II.
Exterior iodine	32.57	32.36	32.30
Iodine as HI	16.28	16.25	—
Chlorine	4.55	4.50	—

By using enough hydriodic acid, long, greenish-black needles

separate, containing no chlorine and giving a green powder; the same substance was deposited from the mother liquors from which the previous compound had crystallised out.

Analysis proved it to be the compound described by Jörgensen, $(C_7H_8N_4O_2, HI)_2, I_6$.

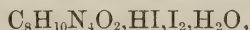
	Calculated.	Found.
Total iodine	73·65	73·68
Exterior iodine	55·24	55·07

This periodide is easily obtained as a dark green powder by simply adding excess of iodine dissolved in potassium iodide solution or hydriodic acid to a solution of theobromine hydrochloride; the precipitate cannot be washed, however, as it is immediately decomposed by water, alcohol, or ether, but the strength of the solutions used does not affect the composition of the precipitate. After draining well on the filter pump, the greater part of the remaining iodine and hydriodic acid can be removed by allowing it to remain over potash or by exposure to air; the compound begins to decompose, however, before the free iodine has completely disappeared. 57·94 and 57·47 per cent. exterior iodine and 75·97 per cent. total iodine were obtained from specimens just beginning to show signs of decomposition, instead of 55·24 and 73·65 per cent.

In some experiments, a mixture of these compounds was obtained, and was recrystallised from weak alcohol containing hydriodic acid and iodine, the last two being used to prevent formation of free theobromine. The acidity of the solution was about 3·5/N and the iodine about N/5. Hydrated crystals were deposited containing no chlorine. Two crops were analysed, and the numbers obtained corresponded with the formula $(C_7H_8N_4O_2, HI)_2, I_4, 2H_2O$.

	Calculated.	Found.	
		I.	II.
Exterior iodine	43·74	43·28	43·24
Iodine as HI	21·87	21·47	21·82
Water	3·11	—	3·38

This compound is homologous with a caffeine periodide,



obtained by Tilden (*Chem. Soc. J.*, 1865, **18**, 99). The two compounds containing chlorine form the intermediate terms of a series, of which $(3C_7H_8N_4O_2, 3HCl)_2, I_6$ and $(3C_7H_8N_4O_2, 3HI)_2, I_6$ would be the extremes.

In the hope of obtaining the latter compound, theobromine was dissolved in a saturated solution of hydriodic acid; green needles gradually separated on exposure to the air, but they contained more iodine than the desired compound.

$(C_7H_8N_4O_2, HI)_4, I_6$ requires a little more exterior iodine, which, perhaps, was lost on drying.

	Calculated for $(3C_7H_8N_4O_2, 3HI)_2, I_2$	Calculated for $(C_7H_8N_4O_2, HI)_4, I_6$	Found.
Exterior iodine . . .	29·14	38·16	37·30
Iodine as HI	29·14	25·44	25·30

This is just half the amount of exterior iodine present in Jørgensen's compound. Perhaps the relationship of these compounds is best shown by the amount of iodine and water attached to 2 mols. of the normal halogen salt, $(C_7H_8N_4O_2, HX)_2$.

1. Those containing hydrochloride have I_2 .
2. That from strong hydriodic acid has I_3 .
3. The hydrated crystals have $I_4 + 2H_2O$.
4. Jørgensen's compound has I_6 .

In conclusion, I must thank Messrs. Howards and Sons, of Stratford, in whose laboratories this work was carried out, for the full facilities so kindly given.

XIII.—*Ethereal Salts of Active and Inactive Monobenzoyl-, Dibenzoyl-, Diphenacetyl- and Dipropionylglyceric acids.*

By PERCY FRANKLAND, Ph.D., B.Sc., F.R.S., and JOHN
MACGREGOR, M.A.

IN pursuing our investigations on the relationship between chemical constitution and optical activity, we have prepared a number of derivatives of active glyceric acid (dextrorotatory) in which the carboxylic hydrogen is replaced by positive radicles, whilst the hydroxylic hydrogen atoms (either one or both) are replaced by the acid radicles benzoyl and phenacetyl. It will be remembered that we have already (Trans., 1893, **63**, 511, 1410, 1419, and 1894, **65**, 750) prepared a number, not only of the ethereal salts of active glyceric acid itself, but also of active diacetylglyceric acid, the compounds under consideration in the present communication being intended to throw further light on the influence exerted on the rotation by making these substitutions in the molecule.

Methylic Dibenzoylglycerate (Active).

This was prepared by running active methylic glycerate from a dropping funnel into twice the calculated quantity of benzoyl

chloride, contained in a flask heated at 120° and finally to 180° by means of an oil bath; a vigorous action takes place, hydrogen chloride being given off. The excess of benzoyl chloride was distilled off under reduced pressure, and the residue then fractionated under diminished pressure; this was attended with some difficulty in consequence of the solidification of the distillate in the lateral tube of the distilling flask. A large part of the liquid passes over at $245-247^{\circ}$. After some hours, the distillate crystallised in tufts of long, flat needles radiating from centres; these crystals are easily soluble in chloroform, acetone, and benzene, soluble also, especially on warming, in methylated spirit, from which recrystallisation can most advantageously be effected, the long, radiating needles having the appearance of thistle-down. The crystals melt at $58-59^{\circ}$.

The crystalline substance was submitted to hydrolysis with alcoholic caustic potash with the following results.

I. 1.2500 gram required 0.6449 gram KOH for hydrolysis.

II. 1.1032 " " 0.5706 " " "

	I.	II.
100 parts by weight of substance required		
KOH for hydrolysis	51.59	51.73

100 parts by weight of methylic monobenzoylglycerate, $C_{11}H_{12}O_5$, require 50.00 parts KOH.

100 parts by weight of methylic dibenzoylglycerate, $C_{18}H_{16}O_6$, require 51.22 parts KOH.

On combustion the following results were obtained.

0.2093 gave 0.5044 CO_2 and 0.0927 H_2O .

	Found.	Calculated for methylic dibenzoylglycerate.	Calculated for methylic monobenzoylglycerate.
Carbon. . . .	65.72	65.85	58.93 per cent.
Hydrogen. .	4.92	4.88	5.35 ,,

Thus, both hydrolysis and combustion clearly show that the substance is pure methylic dibenzoyl and not monobenzoylglycerate.

Owing to the high melting point of this substance, the rotation had to be determined at higher temperatures in a state of fusion, and the rotation for ordinary temperatures deduced by extrapolation.

The density, compared with water at 4° , was determined at 65° and 99° respectively.

$d_{65^{\circ}/4^{\circ}}$ 1.1836. $d_{99^{\circ}/4^{\circ}}$ 1.1581.

from which it appears that the diminution in density proceeds by 0.00075 for 1° rise in temperature.

The substance was submitted to polarimetric examination at the following temperatures in a tube 44 mm. long, placed in an air chamber surrounded by a water jacket.

Temp.	Observed rotation. α_D in 44 mm. tube.	Density compared. with water at 4°.	$[\alpha]_D$.
80.5°.....	+10.26°	1.1720	+19.89°
77.0	10.51	1.1746	20.33
74.0	10.67	1.1769	20.60
71.5	10.79	1.1787	20.80
67.0	11.10	1.1821	21.33
63.5	11.30	1.1847	21.67
59.5	11.57	1.1877	22.13

On plotting out the above figures on a diagram (see p. 122) in which the specific rotations are represented by ordinates and the temperatures of observation as abscissæ, it is found that the observed specific rotations lie almost exactly on a straight line, from which by extrapolation the value for the specific rotation at 15° can be obtained as $[\alpha]_D = +26.89^\circ$. This value may therefore serve for purposes of comparison with active compounds which have had their rotation determined at that temperature.

Methylic Dibenzoylglycerate (Inactive).

This was prepared in substantially the same way as the active compound above. The solutions in methylated spirit exhibited less tendency to crystallise than similar solutions of the active compound, but ultimately very similar crystals, long needles 1 inch in length and radiating from centres, were obtained; these melted at 44–46°, or about 14° below those of the active compound.

The following results were obtained on combustion.

0.2483 gave 0.5978 CO₂ and 0.1093 H₂O. C = 65.66; H = 4.89.

Methylic dibenzoylglycerate, C₁₈H₁₆O₆, requires C = 65.85; H = 4.88 per cent.

The crystals are soluble in the same solvents as those of the active compound.

The molecular weight of this compound, as determined by the cryoscopic method, has been ascertained in benzene, nitrobenzene, ethylene dibromide, and acetic acid solutions (see next paper, p. 123). In these solutions, there is no evidence of the existence of the double molecules corresponding to a racemate, the cryoscopic values for the molecular weight being essentially similar to those obtained for the active methylic dibenzoylglycerate.

Ethylic Dibenzoylglycerate (Active).

This was prepared in the same way as the corresponding methylic compound, by running the active ethylic glycerate into an excess of benzoyl chloride heated to 149—175°. On subsequent fractionation, the greater part distilled over under diminished pressure at 240—260°, and eventually the true boiling point was found to lie between 254° and 258° under about 10 mm. pressure.

0.2498 gave 0.6096 CO₂ and 0.1185 H₂O. C = 66.56; H = 5.27.

C₁₉H₁₈O₆ requires C = 66.67; H = 5.26 per cent.

During the severe weather of the last winter this liquid began to crystallise, and by means of these crystals it was found possible to start its crystallisation in strong alcoholic solution.

A further quantity of this active ethylic dibenzoylglycerate was subsequently prepared with the object of obtaining it, if possible, without distillation. The excess of benzoyl chloride was removed by distillation under diminished pressure, and the residue in the flask was dissolved out with alcohol, but the alcoholic solution could not be brought to crystallise even on sowing with some crystals of the previous preparation. The alcohol was, therefore, distilled off, and the residue, after being washed with a solution of sodium carbonate to remove any benzoic acid that might have been formed from the benzoyl chloride, was dissolved in ether and washed with water. The ethereal solution was evaporated, and the residue placed in a vacuum desiccator, a crystal of the previous preparation being added; crystallisation could, however, not be induced. This undistilled product was also submitted to combustion and to polarimetric examination in benzene solution; these determinations, however, showed that it was of inferior purity and inferior rotatory power to the preparation obtained by distillation. The product was therefore distilled under diminished pressure, and in the distillate crystallisation was induced by sowing with a crystal from the previous preparation. The crystals, which are needles radiating from centres, melt at 25°; they are much more soluble in alcohol than the corresponding methyl compound.

0.2522 gave 0.6144 CO₂ and 0.1192 H₂O. C = 66.44; H = 5.25.

C₁₉H₁₈O₆ requires C = 66.67; H = 5.26 per cent.

The optical activity of this crystalline specimen was determined in benzene solution, and found to be the same as that exhibited by the benzene solution of the first preparation, which had at the time only been obtained in the liquid state.

Thus, the liquid ethylic dibenzoylglycerate obtained in the first preparation by distillation alone, and that obtained in the second

preparation by distillation and subsequent crystallisation were of equal purity, as determined both by combustion and by polarimetric observation.

The density, compared with water at 4°, was determined at 60° and 98·5° respectively.

$d_{15^\circ/4^\circ}$ 1·2010. $d_{60^\circ/4^\circ}$ 1·1596. $d_{98\cdot5^\circ/4^\circ}$ 1·1282.

The substance was submitted to polarimetric examination at the following temperatures.

Temp.	Observed rotation. α_D in 44 mm. tube.	Density compared with water at 4°.	$[\alpha]_D$.
83·0°.....	+10·02°	1·1407	+19·95°
60·0	11·49	1·1596	22·52
49·5	12·11	1·1693	23·53
22·0	13·65	1·1946	25·96
16·5	13·87	1·1996	26·28

On plotting the above figures on a diagram (see p. 122), it is found that the specific rotations for the temperatures from 83° to 49·5° lie almost exactly on a straight line, whilst the line joining the values for the lower temperatures exhibits a very slight but distinct droop. Thus, if the value of the specific rotation for 16·5° be calculated from the change in rotation between the higher temperatures of observation, the following values are obtained.

Value of $[\alpha]_D$ at 16·5°, calculated from specific rotations observed at

	Temperatures.
+27·39°.....	83—60·0°
+27·06	83—49·5
+26·50	83—22·0

which values depart, therefore, but slightly from the actually observed value for 16·5°, which was found to be $[\alpha]_D = +26\cdot28^\circ$.

On further extrapolating the value of $[\alpha]_D$ for 15° from the values actually obtained for 22° and 16·5°, the result is

$$[\alpha]_D = +26\cdot37^\circ \text{ for } 15^\circ.$$

which is only 0·5° inferior to the specific rotation calculated for the methylic compound at the same temperature. In thus extrapolating, it is difficult to know which part of the line to calculate from; thus, in the above we have taken as the basis of calculation the variation in rotation between 22° and 16·5°, a range of temperature which is wholly below the melting point of the compound, namely, 25°. A more rational mode of extrapolation would appear to be to calculate from ranges of temperature which bear the same relationship to the melting points of the two compounds. Thus, the methylic compound melts at 59°, and the ethylic at 25°; we should,

therefore, calculate in the case of the former from the variation in observed specific rotation between 80.5° and 59.5° , whilst in the case of the ethylic salt from the variation between 49.5° and 22° . Calculating in this way, the values become

		$[\alpha]_D$ for 15° .
Methylic dibenzoylglycerate	+26.89
Ethylic	„	+26.58

In consequence of the very slight difference between the specific rotations of methylic and ethylic dibenzoylglycerates at the temperatures referred to above, we thought it desirable to ascertain their rotations at a much higher temperature, and for this purpose we passed a current of aniline vapour through the jacket chamber surrounding the internal metal tube in which the glass polarimeter tube is placed. In this way, a constant temperature of 183° was obtained in the internal tube, but as at this temperature it would have been impossible to use the india-rubber rings, with which we ordinarily bring a gentle pressure to bear on the glass discs closing the ends of the polarimeter tube, we employed instead small spiral springs of copper wire, which answered the purpose admirably.

The following results were obtained—

Methylic dibenzoylglycerate.	Ethylic dibenzoylglycerate.
$\alpha_D = +4.12^\circ$. l 44 mm.	$\alpha_D = +4.02^\circ$. l 44 mm.
$d_{183^\circ/4^\circ}$ 1.0951.	$d_{183^\circ/4^\circ}$ 1.0599.
$[\alpha]_D = \frac{4.12}{1.0951 \times 0.44} = +8.55^\circ. \quad [\alpha]_D = \frac{4.02}{1.0599 \times 0.44} = +8.62^\circ.$	
at 183° .	

The specific rotations of these compounds at this high temperature may also be arrived at by extrapolation from the observations made at lower temperatures, and these calculated values are in both cases most remarkably concordant with the above experimental results; thus, the extrapolated values are for 183°

Methylic dibenzoylglycerate	$[\alpha]_D = +9.01^\circ$
Ethylic	„	„ = +8.78

In order to ascertain whether exposure to this high temperature had permanently altered the rotatory power of these compounds, the rotations were again taken in the same specimens at one of the lower temperatures at which they had been previously determined, with the result that precisely the original figures were obtained.

We have thus shown that the rotation of these two compounds is exceedingly sensitive to temperature, $[\alpha]_D$ at 15° being in each case three times as great as it is at 183° . (See also diagram, p. 122).

Propylic Dibenzoylglycerate (Active).

This was prepared on the same lines as the corresponding methylic and ethylic compounds. The active propylic glycerate was run into twice the calculated quantity of benzoyl chloride at 140° , and the mixture then raised to 180° . After removing the excess of benzoyl chloride by distillation, much difficulty was experienced in distilling the residue at a low pressure, in consequence of violent bumping, nor was this tendency to bump removed by dissolving the ethereal salt in ether and then washing with a solution of sodium carbonate. Ultimately, after repeated fractionation, the main distillate passed over between 267° and 269° .

This product, on combustion, yielded the following results.

- I. 0.2436 gave 0.5992 CO_2 and 0.1221 H_2O . C = 67.09; H = 5.57.
 II. 0.2341 „ 0.5769 „ „ 0.1191 „ C = 67.21; H = 5.65.
 $\text{C}_{20}\text{H}_{20}\text{O}_6$ requires C = 67.42; H = 5.62 per cent.

The density, compared with water at 4° , was determined at 15° , 25° , 60° , and 98.5° ,

$d\ 15^{\circ}/4^{\circ}$	1.1807;	$d\ 60.0^{\circ}/4^{\circ}$	1.1399;
$d\ 25^{\circ}/4^{\circ}$	1.1727;	$d\ 98.5^{\circ}/4^{\circ}$	1.1079.

from which it appears that the diminution in density proceeds by 0.00080 for 1° rise in temperature between 15° and 25° , by 0.00094 for 1° between 25° and 60° , and by 0.00083 for 1° between 60° and 98.5° .

The substance was submitted to polarimetric examination at the following temperatures in a tube 44 mm. long, placed in an air chamber surrounded by a water jacket.

Temp.	Observed rotation α_D in 44 mm. tube.	Density compared with water at 4° .	$[\alpha]_D$.
19.5°	$+10.73^{\circ}$	1.1771	$+20.71^{\circ}$
34.0	10.10	1.1642	19.71
38.0	9.96	1.1605	19.50
48.0	9.53	1.1511	18.81
56.0	9.10	1.1436	18.08
68.2	8.47	1.1331	16.99
78.0	8.02	1.1250	16.20
87.0	7.54	1.1175	15.34

These figures have been plotted on a diagram (see p. 122), from which it appears again that the line joining the specific rotations taken at the higher temperatures is almost straight, but that it drops slightly with the lower temperatures.

In extrapolating the value of $[\alpha]_D$ for 15° , we have no melting point to take into consideration, as we have only had to deal with

this substance in the liquid state; we may therefore reasonably calculate from the variation in specific rotation observed between 38° and 19.5° , from which results the value

$$[\alpha]_D = +21.00 \text{ for } 15^{\circ}.$$

The rotation of the propylic is thus markedly inferior to that of either the methylic or ethylic compounds.

Methylic Diphenylacetyl-glycerate (Active).

The method of preparation was similar to that employed in the case of the other ethereal salts described above. The active methylic glycerate was run into a large excess of the phenylacetyl chloride; the action appeared to commence at 80° , becoming more vigorous at 105° ; the temperature was finally raised to 160° . After the excess of phenylacetyl chloride had been removed by distillation under diminished pressure, the residue was washed with a warm solution of sodium carbonate, extracted with ether, separated, and the ethereal solution washed with water. The ether was then removed by distillation, and the residual liquid fractionated at low pressure, the main distillate being obtained at 265 – 273° . This distillate was again washed with sodium carbonate solution, extracted with ether, shaken up with animal charcoal, as it was slightly coloured, and then dried in a vacuum desiccator. A combustion made with this product showed it to be impure methylic diphenylacetyl-glycerate. It was further purified by repeated distillation in a vacuum, the boiling point being 266 – 270° under 17 mm. pressure.

On combustion, the following results were obtained.

0.2385 gave 0.5877 CO_2 and 0.1231 H_2O . $\text{C} = 67.20$; $\text{H} = 5.73$.

$\text{C}_{20}\text{H}_{20}\text{O}_6$ requires $\text{C} = 67.41$; $\text{H} = 5.62$ per cent.

The density was determined at the following temperatures

$d_{14.2^{\circ}/4^{\circ}} 1.1975$; $d_{41^{\circ}/4^{\circ}} 1.1737$; $d_{80^{\circ}/4^{\circ}} 1.1404$.

from which it appears that the diminution in density proceeds by 0.00089 for 1° rise in temperature between 14.2° and 41° , and by 0.00085 for 1° between 41° and 80° .

Polarimetric determinations were made at the following temperatures.

Temp.	Observed rotation, α_D in 92.35 mm. tube.	Density compared with water at 4° .	$[\alpha]_D$.
14.5° — -17.76°	1.1972	-16.06°
34.0 — 35.0°	-16.62	1.1794	-15.25
45.5 — 46.5	-16.03	1.1694	-14.84
49.5 — 50.5	-15.88	1.1660	-14.74
61.0 — 62.0	-15.38	1.1563	-14.40
69.0 — 70.0	-15.08	1.1495	—
77.5 — -14.88	1.1427	—

Thus the introduction of the two phenylacetyl groups has an entirely different effect from the introduction of the two benzoyl groups, for whilst methylic dibenzoylglycerate is strongly dextro-rotatory, the diphenylacetyl-glycerate is lævorotatory, in fact even more so than methylic diacetyl-glycerate. This profound difference in the rotatory effect produced by the benzoyl and phenylacetyl-groups respectively will be again referred to later (see p. 119).

Although the diphenylacetyl-glycerate resembles the diacetyl-glycerate so closely in its rotation, there is one point in which it strikingly differs, and that is in the sensitiveness of the rotation to temperature; thus, from the above table it will be seen that the lævorotation becomes diminished with rise of temperature, whilst in the case of the diacetyl-glycerates, as we have already shown (Trans., 1894, 65, 765), the lævorotation increases with increase of temperature, the same being true of the glycerates themselves. The dibenzoyl-glycerates, again, have their dextrorotation diminished with increase of temperature.

These remarkable differences in behaviour with regard to temperature obviously indicate that the dissymmetry of the molecule which leads to the lævorotation of the glycerates and diacetyl-glycerates becomes exaggerated with rise of temperature, whilst the dissymmetry of the molecule which occasions the lævorotation of the diphenylacetyl-glycerate diminishes with increase of temperature, and similarly the dissymmetry which brings about the dextrorotation of the dibenzoyl-glycerates becomes moderated by rise of temperature.

Methylic Monobenzoylglycerate (Active).

The active methylic glycerate was mixed with the calculated quantity of benzoyl chloride in the cold. There was no visible action until the mixture was heated to 83° , and it became vigorous at 100° ; the oil-bath was finally raised to 180° , and maintained there for 20 minutes. The product, after being washed with sodium carbonate solution, and with water, was put into a vacuum desiccator, but crystallisation did not ensue. Numerous unsuccessful attempts were made to obtain crystals by using the most varied solvents, in conjunction with a freezing mixture; benzene, aldehyde, chloroform, toluene, aniline, ether, acetone, methylated spirit, propylic alcohol, carbon tetrachloride, and light petroleum were all employed, to no purpose. In light petroleum, the liquid was only very slightly soluble.

The liquid was submitted to combustion, with the following results.

0.2368 gave 0.5120 CO_2 and 0.1072 H_2O . C = 58.97; H = 5.03.

Methylic monobenzoylglycerate, $\text{C}_{11}\text{H}_{12}\text{O}_5$, requires C = 58.93; H = 5.36 per cent.

The liquid, which analysis had thus shown to be pure methylic monobenzoylglycerate, was examined with the polarimeter.

$$\alpha_D = +5.95^\circ; t = 13^\circ; d_{13^\circ/4^\circ} = 1.2655; l = 50 \text{ mm.}$$

It was then distilled under a reduced pressure of 10 mm., when about one-half of it passed over between 180° and 240° .

This distillate, on polarimetric examination, gave the following results.

$$\alpha_D = +7.13^\circ; l = 50 \text{ mm.}; t = 13^\circ.$$

Thus this distillate possessed a considerably higher dextrorotation than the original liquid from which it was obtained, clearly pointing, therefore, to the fact that the original liquid was a mixture of the two possible isomeric methylic monobenzoylglycerates, and from our subsequent experiences with the ethylic compound, there can be little doubt that the more volatile part is the α -modification with the higher dextrorotation, whilst the β -compound with the higher boiling point, and which remained for the most part in the distilling flask, must have a lower dextrorotation, or even a levorotation.

The quantity of material at our disposal was not sufficient to enable us to obtain either of these isomers in a pure state, so that for the present we have had to be content with having indicated this probable relationship between their rotations, namely, *that the methylic α -monobenzoylglycerate is dextrorotatory, but much less so than methylic dibenzoylglycerate, whilst methylic β -monobenzoylglycerate is certainly less dextrorotatory than the α -compound, and possibly even levorotatory.* (For another possible explanation of these phenomena see p. 115.)

Methylic Monobenzoylglycerate (Inactive).

This was prepared in the same way as the active compound, only using inactive methylic glycerate. On drying the product, the ethereal solution of which had been washed with sodium carbonate solution and water in the desiccator, it became pasty and turbid, in consequence of the appearance of small crystals, the quantity of which increased after prolonged standing; a large proportion of the material, however, still remained as a viscid liquid.

The crystals were found to be very soluble in alcohol, chloroform, and acetone, but recrystallisation from hot benzene proved most serviceable for their purification; in this way the crystals are obtained in small, nodular groups, exhibiting a radiated structure. The melting point of the purified crystals was $92.5-93.5^\circ$.

0.2431 gave 0.5213 CO_2 and 0.1170 H_2O . $\text{C} = 58.48$; $\text{H} = 5.35$.
Methylic monobenzoylglycerate, $\text{C}_{11}\text{H}_{12}\text{O}_5$, requires $\text{C} = 58.93$; $\text{H} = 5.36$ per cent.

The product was again recrystallised from benzene, after which the melting point was found to be $92.5-93^{\circ}$, and on combustion the following results were obtained.

0.2112 gave 0.4530 CO_2 and 0.1039 H_2O . $\text{C} = 58.50$; $\text{H} = 5.47$.
Methylic monobenzoylglycerate, $\text{C}_{11}\text{H}_{12}\text{O}_5$, requires $\text{C} = 58.93$; $\text{H} = 5.36$ per cent.

The substance was again recrystallised, and another combustion made.

0.1197 gave 0.2570 CO_2 and 0.0594 H_2O . $\text{C} = 58.55$; $\text{H} = 5.51$.
 $\text{C}_{11}\text{H}_{12}\text{O}_5$ requires $\text{C} = 58.93$; $\text{H} = 5.36$ per cent.

As already pointed out in the case of the active compound, there should be two methylic monobenzoylglycerates, but whether the crystals thus obtained are the α - or the β -compound we have not yet directly determined; from the fact, however, that the crystals appeared in the originally liquid product, and that a large portion of the latter permanently remained in the liquid state, it would appear probable that both the α - and the β -compounds had been formed in the reaction, and that the one was crystallisable, and the other not. It may further be suggested that, by analogy, the crystallisable substance is probably the β -, and the uncrystallisable the α -, compound; thus α -chloropropionic acid is a liquid boiling at 186° , whilst β -chloropropionic acid is a solid, the melting point of which is variously given as $35.5-41^{\circ}$ by Krestovnikoff (*J. Russ. Chem. Soc.*, **11**, 248), and 58° by Richter (*Zeit. f. Chem.*, **1868**, 451); again α -chlorobutyric acid is a viscid liquid (Markovnikoff, *Annalen*, 1870, **153**, 241), whilst β -chlorobutyric acid is a crystalline body, melting at $98-99^{\circ}$ (Markovnikoff, *Zeit. f. Chem.*, **1868**, 621). Similarly α -bromopropionic acid is a liquid boiling at 205.5° , and solidifying at -17° (Kekulé, *Annalen*, 1864, **130**, 16), whilst β -bromopropionic acid is a solid, melting at 61.5° (Richter, *Zeit. f. Chem.*, **1868**, 449).

Ethylic Monobenzoylglycerate (Active).

This was prepared in the same way as the two methylic monobenzoylglycerates described above. After washing the crude product with sodium carbonate solution and water, it was placed in the vacuum desiccator, in which, after six weeks, it began to crystallise, but the greater part remained liquid. The crystals were pressed between filter paper, and dissolved in hot, light petroleum, from which, on cooling, radiating needles were obtained, melting at 62° . Still finer crystals were obtained from petroleum spirit (b. p. $80-117^{\circ}$).

Thus in this case again it would appear that both the α - and the β -compounds are formed in the reaction, and that one of these is

crystallisable, and the other not, and for the reasons given above, the crystallisable one is in all probability the β -compound.

The above crystals were submitted to combustion, with the following results.

0.2503 gave 0.5527 CO_2 and 0.1332 H_2O . $\text{C} = 60.22$; $\text{H} = 5.91$.

0.2293 „ 0.5057 „ „ 0.1220 „ $\text{C} = 60.15$; $\text{H} = 5.91$.

$\text{C}_{12}\text{H}_{14}\text{O}_5$ requires $\text{C} = 60.50$; $\text{H} = 5.88$ per cent.

The crystalline ethylic monobenzoylglycerate was examined polarimetrically in a state of fusion, at the following temperatures.

Temp.	Observed rotation, α_D , $l = 44 \text{ mm.}$	Density, $t^\circ/4^\circ$.	$[\alpha]_D$.
67.0°	-4.98	1.1547	-9.80°
78.5	-4.88	1.1438	-9.70
88.3	-4.88	1.1344	-9.77

Thus the solid ethylic monobenzoylglycerate, which is presumably the β -compound, has a strong lævorotation, which, moreover, remains practically unaltered by change of temperature, and thus differs markedly from all the disubstituted ethereal salts of glyceric acid which we have examined.

The liquid portion of the crude ethereal salt, from which the above solid ethylic β -monobenzoylglycerate had crystallised, was examined in the polarimeter, and was found to possess a dextrorotation. This is, therefore, as in the case of the methylic monobenzoylglycerate, consistent with the supposition that there were two ethylic monobenzoylglycerates formed, of which the solid one (doubtless the β -compound) was obtained in a pure state, and was found to be lævorotatory, whilst the liquid one (doubtless the α -compound) is dextrorotatory.

We would, however, point out that the facts also admit of another explanation, namely, that whilst the solid ethylic monobenzoylglycerate possesses the lævorotation given above, the dextrorotation of the liquid from which it separated *may* be due to ethylic dibenzoylglycerate. A similar explanation would also fit the facts in the case of the methylic compound. We cannot positively decide between these two alternative hypotheses until we have prepared these compounds on a larger scale.

Particularly interesting with regard to the solid ethylic monobenzoylglycerate are the circumstances (1) that its specific rotation is almost identical with that of ethylic glycerate itself (for a fuller discussion of this point see p. 120), and (2) that the specific rotation is extremely insensitive to temperature. This insensitiveness is evident from the figures given above, but we have submitted it to a still more severe test by determining the specific rotation* at 136 — 137°

* The ethylic monobenzoylglycerate used in this experiment was not quite pure,

(using the vapour of xylene in the jacket-tube of the polarimeter), with the following result.

$$\alpha_D = -4.22^\circ; t = 136.5^\circ; l = 44 \text{ mm}; d \ 136.5^\circ/4^\circ = 1.0886;$$

$$[\alpha]_D = \frac{-4.22}{0.44 \times 1.0886} = -8.81^\circ \text{ at } 136.5^\circ.$$

As pointed out in the footnote below, the substance used for this experiment was not quite pure, its rotation at 71° being slightly below what it should be; on increasing the specific rotation at 136.5° in the proportion

$$9.07 : 9.75 :: 8.81 = 9.47,$$

we obtain the corrected $[\alpha]_D = -9.47^\circ$ at 136.5° , or almost exactly the same figure as for the lower temperatures at which the observations were previously made. The specific rotation of this ethylic monobenzoylglycerate is thus almost wholly independent of temperature, our experiments showing that it suffers only the most trivial diminution in value between 67° and 136.5° .

The relationship between ethylic glycerate and ethylic monobenzoylglycerate is thus a very remarkable one, for whilst the molecular dissymmetry of the latter remains practically constant at all temperatures, the molecular dissymmetry of the former (leading to lævo-rotation) increases with the temperature, and at 15° its molecular dissymmetry (as measured by specific rotation) happens to be equal to the uniform molecular dissymmetry of the ethylic monobenzoylglycerate molecule. Thus we have formerly (*Trans.*, 1894, **65**, 769) shown that the specific rotation (lævo) of ethylic glycerate increases by 0.033° for 1° rise in temperature, so that assuming this increase to proceed uniformly, at 136.5° , the specific rotation of ethylic glycerate would be 13.19° , and therefore greatly in excess of that of ethylic monobenzoylglycerate. The exact temperature, in fact, at which coincidence between their specific rotations should take place is 33.8° . These relations strikingly indicate the importance of taking into account temperature in connection with the comparison of the specific rotations of different active substances.

Methylic dipropionylglycerate (Active).

The method of preparation was the usual one of running the glycerate into excess of the acid chloride, but a difficulty arose in consequence of the propionyl chloride containing phosphorus com-

having suffered slight decomposition through a distillation to which it had been submitted, as was shown by its rotation at 71° being $\alpha_D = -4.59^\circ$, $l = 44 \text{ mm.}$,

$$d \ 71^\circ/4^\circ \ 1.1509; [\alpha]_D = \frac{-4.59}{0.44 \times 1.1509} = -9.07^\circ, \text{ instead of } [\alpha]_D = -9.75^\circ,$$

the figure previously found with the pure substance.

pounds, which it appears to be practically impossible to remove, owing to the proximity of their boiling points (propionyl chloride b.p. 80° , PCl_3 b.p. 76° , POCl_3 b.p. 107°). On examining the crude product, it was found to be slightly dextrorotatory and to fume in contact with air; on refractionating, the lower distillate, which fumed, showed a high dextrorotation, whilst the higher fraction had a lævoration. As it was found impossible to entirely remove the fuming liquid by fractionation, the lævorotatory compound was washed successively with a solution of sodium carbonate and with water, then dried in a vacuum desiccator, and subsequently distilled; the distillate thus obtained did not fume, and gave the following polarimetric result.

$$\alpha_D = -11.5^{\circ}; l = 99.2 \text{ mm. at } 14.8^{\circ}.$$

This liquid was again distilled, but the amount of distillate obtained was so small that the rotation could not be ascertained with the requisite accuracy, but it was approximately $\alpha_D = -11.6$ — 11.9° ($l = 99.2$ mm.). The dextrorotation of the fuming liquid referred to above was doubtless due to the presence of chlorine derivatives of glyceric acid formed by the action of the phosphorous compounds in the propionyl chloride used.

A second preparation again yielded a crude product which fumed in the air, and this instead of being distilled was washed with a solution of sodium carbonate as described above. By repeated fractionation of this washed product, a liquid was obtained having a rotation

$$\alpha_D = -12.2^{\circ} \quad (l = 99.2 \text{ mm.}) \text{ at } 14.2^{\circ}.$$

this was again fractionated, and the distillate then gave substantially the same rotation as before, thus

$$\alpha_D = -6.23^{\circ} \quad (l = 50 \text{ mm.}) \text{ at } 15.2^{\circ}.$$

The rotation was found to be considerably influenced by temperature, and, as in the case of the diacetylglycerates, the rotation increases with rise of temperature. The specific rotation may be calculated from the above figures, and the density, which was found to be $d_{15^{\circ}/4^{\circ}} 1.1349$, thus

$$[\alpha]_D = \frac{-6.23}{0.5 \times 1.1349} = -10.97^{\circ}.$$

This rotation is slightly inferior to that of methylic diacetylglycerate, which we have previously shown (Trans., 1893, **63**, 1430) to be $[\alpha]_D = -12.04^{\circ}$. It is to be anticipated, therefore, that the dibutyrylglycerates will exhibit a further diminution in lævoration and so on for the series of fatty acid radicles. Although the fact that the rotation obtained was essentially the same for the two

separately prepared specimens of methylic dipropionylglycerate points to the rotation being correct, still we give the figure with some reserve in consequence of the phosphorus compounds present in the propionyl chloride employed having conceivably interfered with the optical purity of the product.

On combustion the following results were obtained.

0.2912 gave 0.5478 CO₂, and 0.1818 H₂O; C = 51.30; H = 6.94.

C₁₀H₁₆O₆ requires C = 51.72; H = 6.90 per cent.

Again for hydrolysis with alcoholic potash.

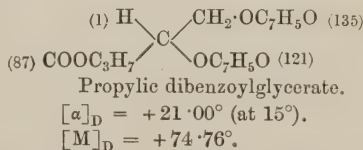
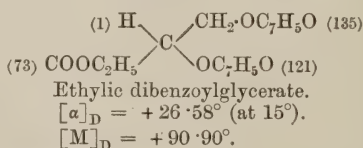
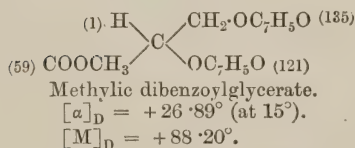
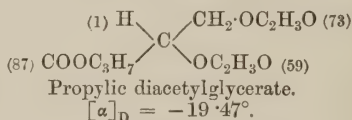
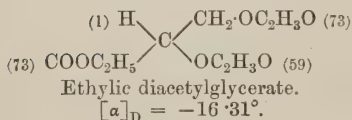
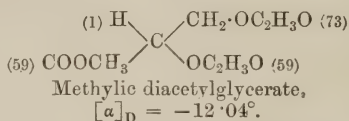
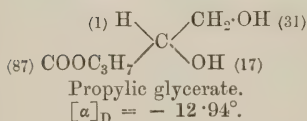
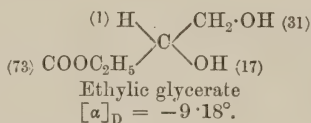
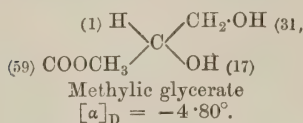
I. 1.0506 gram required 0.7566 gram KOH = 72.01 per cent.

II. 0.9426 " " 0.6798 " " = 72.12 "

Calculated for methylic dipropionylglycerate = 72.41 "

Summary and Conclusions.

(1.) Whilst the ethereal glycerates are lævorotatory, and the diacetylgycerates more lævorotatory still, the dibenzoylgycerates are powerfully dextro-rotatory, thus



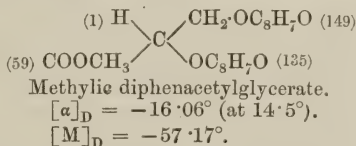
(2.) We have already shown (Trans., 1893, 63, 1415, and 1894,

65, 754) that in the series of the glycerates and the diacetylglycerates respectively, the rotations rise with the positive radicle, attaining in each series a maximum at the isobutyl compound. In the series of the dibenzoylglycerates, on the other hand, the rotations diminish from the methylic salts onwards, the rotations of the methylic and ethylic salts being almost identical, but considerably greater than the normal propylic.

As the dextrorotation is conditioned by the benzoyl groups, whilst the positive radicles alone condition a negative rotation of the molecule, we should anticipate that by increasing the magnitude of the positive radicle the tendency towards a negative rotation would be increased, or in other words that the positive rotation would be diminished, and this is actually found to be the case. It would, however, have been anticipated that this diminution in positive rotation should have proceeded more regularly, and that the positive rotation of ethylic dibenzoylglycerate should have been considerably inferior to that of the methylic compound.

If this line of argument be correct it is further to be anticipated that this diminution in the positive rotation of the dibenzoylglycerates will continue until the isobutylic compound is reached, beyond which the positive rotation should again increase. This point we have not yet had time to determine.

(3.) Whilst the presence of the two benzoyl groups thus conditions a positive rotation, the result is entirely otherwise if two phenacetyl groups be introduced instead. Thus we have found methylic diphenacetylglycerate to be lævorotatory



In fact this compound has almost exactly the same rotation as ethylic diacetylglycerate, and a little higher rotation than that of methylic diacetylglycerate.

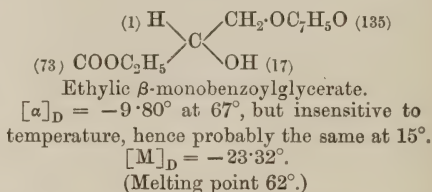
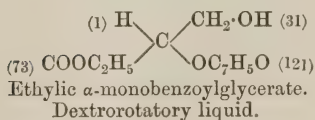
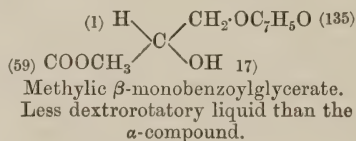
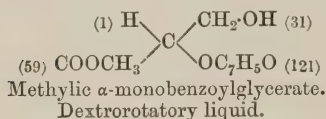
This is a most striking illustration of what we have before called attention to (Trans., 1893, 63, 535), that the rotation is more powerfully influenced by the qualitative character than by the mere mass of the groups attached to the asymmetric carbon atom.

(4.) We have also prepared some of the monobenzoylglycerates. Of each of these, there should, obviously, always be two isomeric modifications, according as the benzoyl group enters the glyceric acid molecule in the α - or in the β -position. These compounds were obtained by mixing the calculated quantities of benzoyl chloride and

ethereal salt of glyceric acid and then heating the mixture as long as hydrogen chloride was evolved; both isomers appear in every case to be formed.

In the case of methylic monobenzoylglycerate (active), both isomers being liquid, we have not yet been able to separate them perfectly from each other. We have, however, shown that the lower boiling isomer, which is in all probability the α -compound, has a greater dextrorotation than the higher boiling and, presumably, β -compound; in fact the latter may even be laevorotatory.

A solid methylic monobenzoylglycerate (inactive) was obtained which melted at $92.5-93^\circ$. In the case of ethylic monobenzoylglycerate (active) the higher boiling, and, therefore, presumably β -compound is solid (m. p. 62°), and has been purified by repeated crystallisation. It is laevorotatory, and has almost exactly the same rotation as ethylic glycerate itself.



The almost exact equality between the specific rotations of ethylic glycerate ($[\alpha]_D = -9.18^\circ$) and of ethylic β -monobenzoylglycerate ($[\alpha]_D = -9.80^\circ$) is extremely remarkable, for it would surely be anticipated that the displacement of a single atom of hydrogen by such an enormous group as the benzoyl radicle should produce a profound change in the dissymmetry of the molecule as measured by specific rotation. This replacement of hydrogen by benzoyl, without much effect on the rotation, is only realised in the case of the $\text{CH}_2\cdot\text{OH}$ -group of ethylic glycerate, for, by replacing the H in the OH-group by $\text{C}_7\text{H}_5\text{O}$, the product is dextrorotatory (see ethylic α -monobenzoylglycerate), and, therefore, entirely different, even in the sign of its rotation, from the original ethylic glycerate.

(5.) The remarkable phenomenon of replacement without marked change in rotation is also exhibited in the case of the methylic diphenylacetyl glycerate referred to in (3), for, as there pointed out, the rotation of this compound ($[\alpha]_D = -16.06^\circ$ at 14.5°) differs but slightly from that of methylic diacetyl glycerate ($[\alpha]_D = -12.04^\circ$), although

the constitutional change is of such a profound character as the displacement of two hydrogen atoms by two C_6H_5 -groups.

(6.) Methylic dipropionylglycerate ($[\alpha]_D = -10.97^\circ$), again, exhibited only a very slight difference in rotation from methylic diacetyl-glycerate ($[\alpha]_D = -12.04^\circ$), although the constitutional change is considerable, consisting as it does in the replacement of two atoms of hydrogen by two CH_3 -groups.

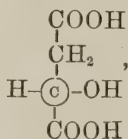
(7.) It is worthy of remark, that in all these cases in which substitution is attended with comparatively little change in rotatory power, the substitution takes place at a point which is comparatively remote from the asymmetric carbon atom; whilst in those cases in which the substitution is so near the asymmetric carbon atom that it is only separated from it by a single atom of oxygen, the change in rotatory power is very considerable. Thus, turning for illustrations of this principle to the experimental material which we have ourselves furnished in this and previous communications, we find

- (1) Passage from glycerates to dibenzoylglycerates causes great change in specific rotation.
- (2) Passage from glycerates to diacetyl-glycerates causes great change in specific rotation.
- (3) Passage from glycerates to diphenylacetyl-glycerates causes great change in specific rotation.
- (4) Passage from lactates to benzoyllactates causes great change in specific rotation.
- (5) " " acetyl-lactates " " "
- (6) " glycerate to α -monobenzoylglycerate causes great change in specific rotation.
- (7) Passage from methylic glycerate to ethylic glycerate causes great change in specific rotation.
- (8) Passage from ethylic glycerate to propylic glycerate causes smaller change in specific rotation.
- (9) Passage from propylic glycerate to isobutylic glycerate causes still smaller change in specific rotation.
- (10) Passage from propylic glycerate to normal butylic glycerate causes practically no change in specific rotation.
- (11) Passage from normal butylic glycerate to heptylic glycerate causes very little change in specific rotation.
- (12) Passage from heptylic glycerate to octylic glycerate causes very little change in specific rotation.
- (13) Passage from methylic dibenzoylglycerate to ethylic dibenzoylglycerate causes practically no change in specific rotation.
- (14) Passage from ethylic glycerate to ethylic β -monobenzoylglycerate causes practically no change in specific rotation.
- (15) Passage from methylic diacetyl-glycerate to methylic diphenylacetyl-glycerate causes very little change in specific rotation.

An exception to the above rule is afforded by the specific rotations of the three dibenzoylglycerates which we have prepared, and in which we found that passage from the methylic to the ethylic com-

pound was attended with less effect on the rotation than passage from ethylic to propylic, although the latter substitution is more remote from the asymmetric carbon atom.

Again, the same phenomenon is exhibited by the extensive material which has been furnished by Walden (*Zeit. physikal. Chem.*, 1895, 17, 264) in connection with the derivatives of malic acid. Thus, bearing in mind the arrangement of the groups around the asymmetric carbon atom,

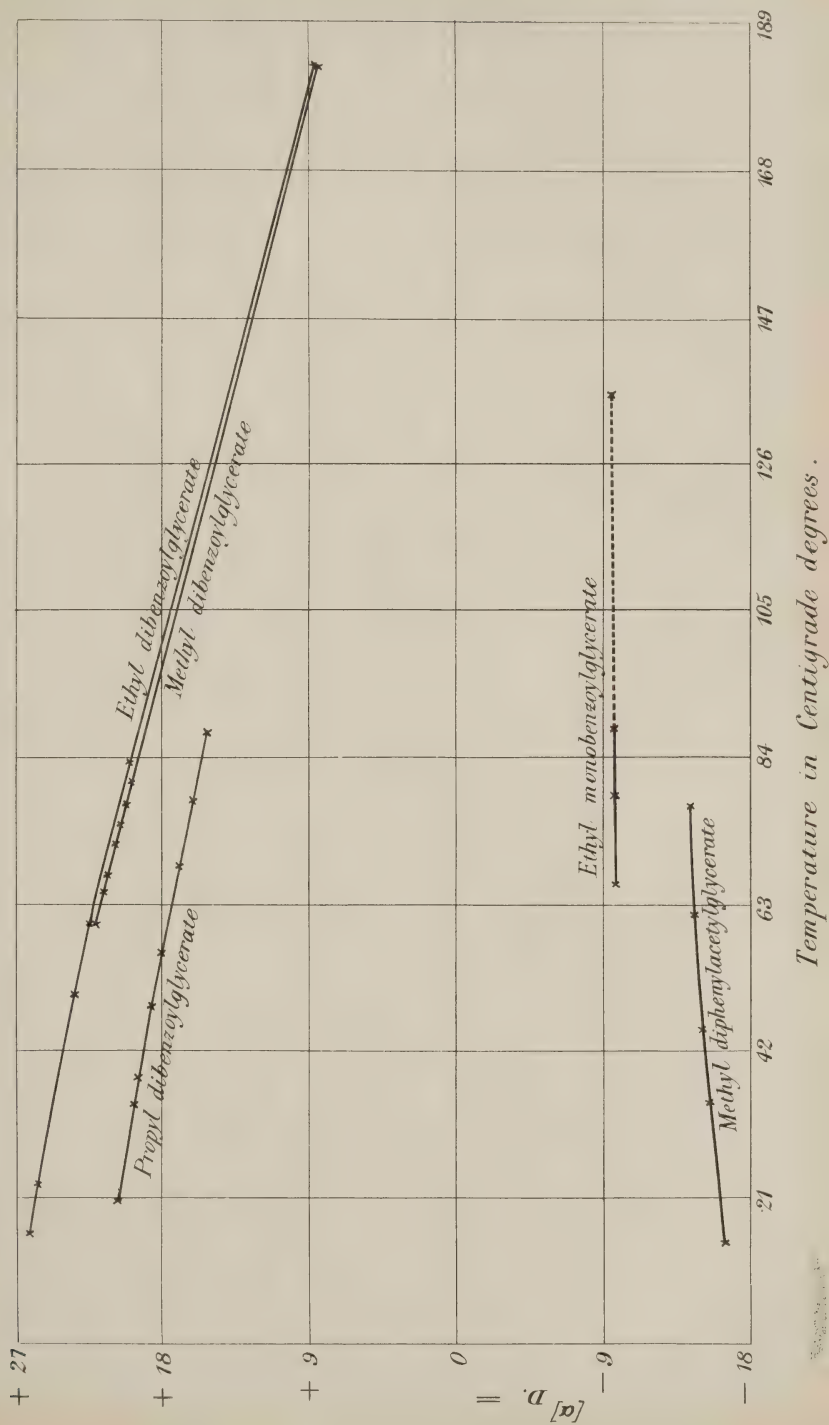


the following results will be seen to show that replacement of the carboxylic hydrogen atoms produces a considerable effect on the rotation; but a much greater effect is obtained by replacing the hydroxylic hydrogen; whilst after this latter hydrogen has been replaced, all further substitutions carried out in the substituting group itself are almost entirely without influence on the rotation.

	[α] _D		[α] _D
Dimethylic malate.....	- 6.85	Dipropylic acetylmalate ...	- 22.85°
Diethylic „	- 10.18	„ chloracetylmalate	- 23.52
Dipropylic „	- 11.62	„ butyrylmalate....	- 22.40
Diisopropylic „	- 10.41	„ isovalerylmalate..	- 21.68
	(about)	„ bromacetylmalate.	- 22.24
Diisobutylic „	- 11.14		
Diamylic „	- 9.92	Diisobutylic acetylmalate...	- 21.88
Dicaprylic „	- 6.92	„ butyrylmalate..	- 21.68
	(about)	„ isovalerylmalate	- 19.91
		„ bromacetylma-	
		late	- 20.38
Dimethylic acetylmalate....	- 22.92		
„ propionylmalate .	- 22.94	Maldiamide	- 38.0*
„ butyrylmalate ...	- 22.44	Malic acid	- 5.75*
„ isobutyrylmalate.	- 22.36	Maldianilide	- 60.0*
„ isovalerylmalate .	- 22.39	Maldi- <i>o</i> -toluide.....	- 66.5*
„ chloracetylmalate	- 23.30	Maldi- <i>p</i> -toluide.....	- 70.0*
„ bromacetylmalate	- 22.40	Mal- β -naphthyl	- 51.5*
Diethylic acetylmalate	- 22.52	Chlorosuccinic acid	+ 52.0*
„ propionylmalate...	- 22.20	„ anhydride... ..	+ 31.0*
„ butyrylmalate....	- 22.22		(about)
„ isobutyrylmalate...	- 21.99	„ chloride	+ 29.53
„ isovalerylmalate...	- 22.07	Dimethylic chlorosuccinate..	+ 41.42
„ bromacetylmalate..	- 22.48	Diethylic „ ..	+ 27.50
„ brompropionylma-		Dipropylic „ ..	+ 25.63
late.....	- 22.48	Diisobutylic „ ..	+ 21.57
„ brombutyrylmalate	- 24.76		(about)
„ bromisobutyrylma-		Diamylic „ ..	+ 21.56
late.....	- 22.57		

* The rotation of these compounds was taken in solution.

INFLUENCE OF TEMPERATURE ON THE SPECIFIC ROTATION OF COMPOUNDS DESCRIBED.

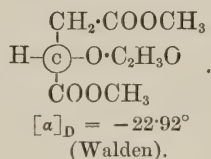
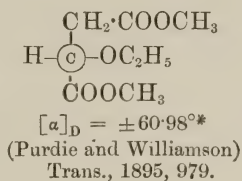
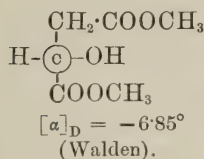




Dimethylic bromosuccinate..	+ 51·18	Dipropylic bromosuccinate..	+ 38·05
Diethylic „ ..	+ 40·96	Diisobutylie „ ..	+ 23·56

Thus in the above series such a change as that from dimethylic acetylmaleate to dimethylic chloracetylmaleate is essentially similar to the change from methylic diacetylglycerate to methylic diphenylacetylglycerate; and in both cases the effect on rotation is remarkably small. In malic acid, the hydroxyl group being directly attached to the asymmetric carbon atom, corresponds to the α -hydroxyl group in glyceric acid, and replacement of this hydrogen in both cases produces a profound change in the rotation. Still more profound is the change in the rotation if the whole of the OH-group is substituted; as, for example, in the passage from dimethylic maleate to dimethylic chlorosuccinate.

Again, it appears that the replacement of the hydroxylic hydrogen by a hydrocarbon radicle produces far more effect on the rotation than the substitution of the same atom of hydrogen by an acid radicle containing the same number of carbon atoms; thus a comparison may be made between



XIV.—*Rotation of Optically Active Compounds in Organic Solvents.*

By PERCY FRANKLAND, Ph.D., F.R.S., and ROBERT HOWSON PICKARD, B.Sc.

IN pursuing the study of the connection between optical activity and chemical composition, the investigation is frequently hampered by the circumstances that the active compounds under examination are solid at those temperatures at which polarimetric observations can be conveniently made, and that the optical activity displayed by the substance in solution is liable to enormous variations according to the particular solvent employed. Great importance, therefore, attaches to the discovery of any relationship between the real optical

* The sign \pm is employed, as it has not yet been determined whether dextro-ethoxysuccinic acid is derived from dextro- or from lævo-malic acid; in either case, however, our statement above is strongly supported by the facts.

activity of a particular substance and the variable activity which it exhibits in different solvents.

This problem has been attacked in a very suggestive way by Freundler (*Thèses présentées à la Faculté des Sciences de Paris*, 1894) in connection with his interesting researches on the derivatives of tartaric acid, and his conclusions are summarised in the two following statements.

“When a solvent gives normal figures for the molecular weight of the dissolved active compound, it does not alter its rotatory power for any concentration.

“On the contrary, if the solvent gives abnormal figures for the rotatory power, it causes the compound to undergo some change, and yields also abnormal cryoscopic and ebullioscopic figures. In this case, the concentration influences $[\alpha]_D$, which departs from the normal value in proportion as the solution is more dilute.”

The latter mode of behaviour is ascribed by Freundler to the operation of a dissociation process in neutral organic solvents analogous to that which takes place in saline solutions.

The double importance of this subject, from the point of view of optical activity on the one hand, and from that of the dissociation theory on the other, appeared to render it highly desirable that the validity of these conclusions should be tested by further experiments, and for which some of the optically active compounds prepared by one of us were particularly well adapted.

The experiments which we have carried out with this object consist, firstly, in the determination of the optical activity of a pure substance in the liquid state, secondly in the determination of its activity at different dilutions in solidifiable solvents, and, thirdly, in the cryoscopic determination of the molecular weight of the active substance in the same solvents at similar dilutions.

The optically active substance which served for the greater number of our experiments was methylic dibenzoylglycerate, which crystallises in beautiful, slender needles melting at 58–59°, and often upwards of an inch in length.

The optical activity and molecular weight of methylic dibenzoylglycerate were determined in the following solvents:—Benzene, acetic acid, ethylene dibromide, and nitrobenzene.

Experiments with Benzene as Solvent.

In order to test the cryoscopic apparatus employed, which was of the ordinary Beckmann type with a thermometer graduated in hundredths of a degree Cent., the following determinations were made with naphthalene.

Cryoscopic Determinations with Naphthalene in Benzene.

Molecular weight of Naphthalene = 128.

Molecular depression for Benzene = 49 (Raoult, *Annales d. Chim. et Phys.*, [6] 2, 1884).

Weight of benzene in grams.	Weight of naphthalene in grams.	Grams of naphthalene in 100 grams of solution.*	Depression of freezing-point in °C.	Molecular weight deduced.
37·4965	0·6345	1·6	0·685	121·1
"	0·7555	1·9	0·810	121·8
"	1·1842	3·0	1·285	120·4
"	1·6545	4·2	1·745	123·9
37·2020	1·6800	4·3	1·770	125·0
37·4965	2·5320	6·3	2·660	124·4
37·2020	3·2540	8·0	3·395	126·3
37·4965	3·3070	8·1	3·440	125·6

The above figures, which approximate to the theoretical molecular weight of naphthalene, show that the arrangement employed was capable of yielding accurate results.

In the next instance, a similar series of cryoscopic determinations was made with active methylic dibenzoylglycerate (derived from dextrorotatory glyceric acid).

Cryoscopic Determinations with Active Methylic Dibenzoylglycerate in Benzene.

Molecular weight of Methylic Dibenzoylglycerate = 328.

Weight of benzene in grams.	Weight of methylic dibenzoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing-point in °C.	Indicated molecular weight.
6·5776	0·1567	2·3	0·370	315·5
"	0·3489	5·0	0·865	300·5
"	0·3787	5·4	0·945	298·6
"	0·5554	7·8	1·360	304·2
"	0·7144	9·8	1·710	311·2
"	0·8863	11·9	2·100	314·4
"	1·1010	14·3	2·595	316·0
"	1·2920	16·4	3·010	319·8
"	1·4439	18·0	3·380	318·2
"	1·8644	22·0	4·320	321·5

* The percentage of substance employed is, throughout the paper, given in terms of 100 parts of the *solution* and not of the *solvent*, as is usually done. The

In this series it will be seen that the indicated molecular weights of the ethereal salt are in all cases decidedly below the theoretical, the values being, on the whole, smallest for the most dilute solutions, and rising with increased concentration.

The molecular weight of an optically active compound at once raises the question as to what is the molecular weight of the corresponding inactive "racemate." This question was discussed many years ago by Perkin (*Trans.*, 1867, **20**, 149), who was, however, unable to obtain the molecular weights of the ethereal salts of tartaric and racemic acids by vapour density determination, but came to the conclusion that their molecular weights must be identical in consequence of the identity of the boiling points of the corresponding ethereal salts of the tartaric and racemic acids. As far as we are aware, however, this point has not yet been investigated by means of cryoscopic and ebullioscopic methods for racemates dissolved in organic liquids.* We proceeded, therefore, to make a similar series

object of this is to render the percentage composition of the solutions submitted to cryoscopic examination directly comparable with that of the solutions examined in the polarimeter.

* Since making these experiments, we find that K. Auwers (*Zeit. physikal. Chem.*, 1894, **15**, 51) has cryoscopically examined methylic and ethylic lactates (inactive of course) in benzene solution, with the following results.

Methylic lactate (inactive), $C_4H_8O_3 = 104$.

Grams of solvent (benzene).	Grams of substance.	Grams of substance to 100 grams solvent.	Observed depression.	Molecular weight deduced.
15·00	0·1050	0·70	0·347	98·9
"	0·2220	1·48	0·662	110·0
"	0·5555	3·70	1·430	127·0
"	1·0205	6·80	2·271	147·0
"	1·3920	9·28	2·801	162·0

Ethylic lactate (inactive), $C_5H_{10}O_3 = 118$.

"	0·0600	0·40	0·183	107·0
"	0·1090	0·73	0·302	118·0
"	0·3258	2·17	0·831	128·0
"	0·6225	4·15	1·463	139·0
"	0·9862	6·57	2·101	153·0
"	1·3265	8·84	2·535	171·0
"	1·5350	10·23	2·945	170·0
"	1·7725	11·82	3·294	176·0

There is no reference made to the possibility of the lactates being present as racemised molecules, and the very high values obtained for the molecular weights are attributed exclusively to the abnormal behaviour which is exhibited by hydroxy-compounds in general. This conclusion can, however, obviously be only provisionally drawn in the absence of any information as to the cryoscopic behaviour of the corresponding active compounds.

of cryoscopic determinations with inactive methylic dibenzoylglycerate, a substance which also crystallises in long, slender needles melting at 44—46°, whilst the active body melts at 58—59°.

The solubility of the active and inactive compounds in alcohol was also found to be very different; thus at 12·8°, 100 parts by weight of methylated spirit dissolves 1·96 part of active, and 5·33 parts of inactive methylic dibenzoylglycerate.

Cryoscopic Determinations with Inactive Methylic Dibenzoylglycerate in Benzene Solution.

Molecular weight of inactive methylic dibenzoylglycerate (calculated as a racemate) = $328 \times 2 = 656$.

Weight of benzene in grams.	Weight of methylic dibenzoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in °C.	Indicated molecular weight.
5·8980	0·2281	3·7	0·600	308·7
8·2791	0·3350	3·8	0·640	309·8
"	0·4602	5·2	0·915	297·7
5·8980	0·4559	7·1	1·240	305·4
8·2791	0·6542	7·3	1·285	301·3
"	0·8111	8·9	1·570	305·7
"	1·0280	11·0	1·980	307·3
"	1·3430	13·9	2·560	310·5
"	1·5917	16·1	3·015	312·4
"	1·8346	18·2	3·445	315·2

The above figures for the molecular weight are obviously substantially the same as those obtained with active methylic dibenzoylglycerate, and clearly indicate that *in the benzene solution the molecules of the oppositely active ethereal salts, which give rise to the inactive compound, are not in combination*. The figures afford, moreover, in their divergence from the calculated weight of the single molecule, a confirmation of the results recorded above for active methylic dibenzoylglycerate.

It will be interesting now to compare with these cryoscopic measurements the polarimetric determinations made with similar solutions of active methylic dibenzoylglycerate in benzene. The results are recorded in the following table (p. 128).

These figures show that the rotation $[\alpha]_D$ of the ethereal salt in benzene solution is greatly in excess of its rotation in the pure state, and, further, that the rotation increases slowly, but unmistakably, with the dilution of the solution. From the diagram given on p. 140, it will be seen that the rate of increase in rotation proceeds very steadily with the dilution until the highest dilution is reached, when

an abrupt rise in the rotation was observed. But, on extrapolation, it is found that, even with infinite concentration, the rotation is considerably in excess of that experimentally obtained with the pure substance in a state of fusion. Thus, on producing the straight line beyond the diagram to 100 per cent. concentration, the value $[\alpha_D] = +33.3^\circ$ is obtained, whilst the rotation of the pure substance at 15° is $[\alpha]_D = +26.89^\circ$.

Rotation of Benzene Solutions of Active Methylic Dibenzoylglycerate.

$[\alpha]_D$ for methylic dibenzoylglycerate in the pure state at $15^\circ \text{C.} = +26.89^\circ$.

Weight of benzene solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Observed rotation, α_D , in 100.47 mm. tube.	Density of solution at temperature of observation compared with water at 4° .	Temperature at which rotation and density were determined.	Specific rotation, $[\alpha]_D$.
4.7633	0.1435	3.0	+ 1.23°	0.8929	14.5°	+ 45.70°
3.4963	0.1641	4.7	1.86	0.8962	16.5	44.01*
3.3259	0.2414	7.2	2.87	0.9017	16.5	43.66
6.2430	1.2191	19.5	7.80	0.9411	15.0	42.26
4.9486	1.6916	34.1	13.76	0.9847	14.5	40.72

EXPERIMENTS WITH ETHYLENE DIBROMIDE AS SOLVENT.

A similar series of experiments was made both with the active and inactive methylic dibenzoylglycerates in ethylene dibromide solution (see next page). The ethylene dibromide employed, both in the cryoscopic and polarimetric determinations, was dried with calcium chloride and redistilled (b. p. 129°). The melting point was 10° .

Thus, in the case of the ethylene dibromide solution there is little or no evidence of dissociation, even with the highest dilutions employed, whilst in the more concentrated solutions the indicated values for the molecular weight are distinctly excessive. The values obtained in the case of the inactive compound are substantially the same as those for the active.

* In order to ascertain whether the rotation is affected by the solution being kept, this particular solution was preserved 18 hours before examination, whilst the other solutions were examined at once. The result shows that no change appears to take place, as the figure obtained falls into line with the others.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoylglycerates in Ethylene Dibromide Solution.

Molecular weight of methylic dibenzoylglycerate = 328.

Molecular depression for ethylene dibromide = 118.

Weight of ethylene dibromide in grams.	Weight of methylic dibenzoylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of the freezing-point in °C.	Indicated molecular weight.
(a). <i>Active Compound.</i>				
9.7573	0.2078	2.0	0.780	322.2
25.2479	0.6784	2.6	0.985	321.9
"	0.9805	3.7	1.415	323.8
"	1.2457	4.7	1.755	331.7
"	1.4982	5.6	2.090	335.0
9.7573	0.6807	6.5	2.470	333.3
"	0.7809	7.4	2.740	344.7
"	0.9238	8.6	3.240	344.8
"	1.0589	9.8	3.695	346.6
25.2479	2.7747	9.9	3.725	348.1
"	2.9323	10.4	3.885	352.7
"	3.1297	11.0	4.155	352.1
"	3.3903	11.9	4.525	350.1
9.7573	1.3553	12.2	4.630	354.0
"	1.7050	14.9	5.745	358.8
(b). <i>Inactive Compound.</i>				
15.7778	0.2125	1.3	0.475	334.6
5.5932	0.0963	1.7	0.580	350.3
15.7778	0.4595	2.8	1.040	330.5
5.5932	0.3107	5.3	1.900	345.0
"	0.4031	6.7	2.450	347.1
"	0.4643	7.6	2.870	341.3
"	0.5596	9.0	3.460	341.2
"	0.7146	11.3	4.290	351.4
"	0.9003	13.8	5.290	359.0

The results given in the table on p. 130 were obtained on examining similar solutions in the polarimeter.

Thus, the rotation for all concentrations is greatly inferior to that exhibited by the pure substance in a state of fusion; there is, moreover, very little variation with the concentration, but such as there is leads to the stronger solutions having a distinctly higher rotation than the weaker ones. This slightly greater rotation is thus obtained in the case of those solutions which yield the markedly high values for the molecular weight as determined by the cryoscopic method.

The relationship between the rotation and concentration is best seen by reference to the diagram on p. 140. By producing the straight line beyond the diagram until a concentration of 100 per cent. is reached, the value $[\alpha]_D = +32^\circ$ is obtained, and which is considerably in excess of that actually yielded by the pure substance.

*Rotation of Ethylene Dibromide Solutions of Active Methylic
Dibenzoylglycerate.*

[α]_D for methylic dibenzoylglycerate in the pure state at 15° = +26·89°.

Weight of ethylene dibromide solution, in grams.	Weight of substance, in grams.	Grams of substance in 100 grams solution.	Observed rotation, α_D , in 100·47 mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Temperature at which rotation was observed.	[α] _D .
10·9492	0·3695	3·3	+1·38°	2·1286	17·5°	+19·18*
13·5373	0·8982	6·6	2·78	2·0749	17·5	20·09*
10·1979	1·1146	10·9	4·36	2·0103	17·0	19·77
16·8104	2·5857	15·4	6·33	1·9494	15·0	21·02
13·8365	3·0936	22·3	9·03	1·8538	17·5	21·69

EXPERIMENTS WITH NITROBENZENE AS SOLVENT.

A similar series of cryoscopic determinations was made both with active and inactive methylic dibenzoylglycerate in nitrobenzene solution. The nitrobenzene employed both in these and in the subsequent polarimetric measurements had a constant boiling point of 207° and melted at 5·4°. The cryoscopic determinations gave very irregular results; we have, however, recorded them in the following table.

The figures from the cryoscopic determinations (next page), although disappointingly irregular, show that the indicated molecular weight is distinctly greater in nitrobenzene than in benzene, many of the values found approximating closely to the theoretical, irrespectively of the concentration. In spite of their irregularity, the general tendency of the figures is to show that with the greatest dilution the molecular weight is lower than the theoretical, and with the highest concentration that it rises above the theoretical.

As regards the indicated molecular weight of the inactive compound, all the values obtained very closely approximate to the theoretical weight of a single molecule, and thus confirm the conclusion arrived at in the case of the benzene and ethylene dibromide solutions, that the oppositely active molecules of which the inactive compound consists are not in combination in the solution.

On now turning to the polarimetric determinations made with the nitrobenzene solution of the active compound, the following results were obtained (see second table on next page).

* These solutions were made up 18 hours before examination with the polarimeter.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoyleglycerate in Nitrobenzene Solution.(a). *Active Compound.*

Molecular weight of methylic dibenzoyleglycerate = 328.

Molecular depression for nitrobenzene = 72.

Weight of nitrobenzene in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in °C.	Indicated molecular weight.
5.2072	0.0925	1.7	0.420	304.5
5.4957	0.2247	3.9	0.900	327.1
5.2072	0.2919	5.3	1.270	317.8
"	0.3780	6.7	1.655	315.8
5.4957	0.4702	7.8	1.910	322.5
5.2072	0.4681	8.3	2.050	315.7
5.4957	0.6501	10.5	2.500	340.7
5.0482	0.6333	11.1	2.665	338.9
5.2072	0.6580	11.2	2.810	323.8
5.4957	0.7367	11.8	2.885	334.4
"	0.8782	13.7	3.495	329.2
5.2072	0.9519	15.4	4.015	327.8
5.0482	0.9642	16.0	4.030	341.2
5.2072	1.0019	16.1	4.200	329.8
5.4957	1.1507	17.3	4.475	336.9

(b). *Inactive Compound.*

5.0764	0.2336	4.4	1.000	331.3
"	0.3536	6.5	1.545	324.6
"	0.4064	7.4	1.760	327.5
"	0.4936	8.8	2.160	324.1
"	0.5452	9.7	2.390	323.6
"	0.6623	11.5	2.860	328.4
"	0.8919	14.9	3.785	334.2
"	1.0563	17.2	4.500	332.9

Rotation of Nitrobenzene Solutions of Active Methylic Dibenzoyleglycerate.[α]_D from ethylic dibenzoyleglycerate in the pure state at 15° C. = +26.89°.

Weight of nitrobenzene solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams solution.	Observed rotation α_D in 100.47 mm. tube.	Density of solution at temperature of observation compared with water at 4°.	Temperature at which rotation was observed.	[α] _D .
6.9157	0.1668	2.4	+0.58	1.2079	15.0	+19.83
4.7130	0.2632	5.5	1.40	1.2082	15.9	20.62
5.9898	0.6795	11.3	2.94	1.2082	16.3	21.33*
5.7157	0.9950	17.4	4.60	1.2096	16.6	21.75
6.6643	1.8694	28.1	7.54	1.2164	15.5	21.99

* This solution was made up 18 hours before polarimetric examination.

From these figures it will be seen that, although the observations were made over a very wide range of concentration, the specific rotation only suffered comparatively slight change. The specific rotation was only about one-half of that exhibited in benzene solution, and was markedly inferior to that possessed by the pure substance in a state of fusion. Moreover, whilst in benzene the rotation increases with the dilution, in nitrobenzene it diminishes. The relationship is best seen from the diagram on p. 140, from which it may also be shown that, by extrapolating, the value for infinite concentration closely approaches, although it is slightly below, the experimental value for $[\alpha]_D$ obtained with the pure substance in a state of fusion. Thus, by producing the straight line beyond the diagram until it reaches a concentration of 100 per cent., the value obtained for $[\alpha]_D$ is $+25^\circ$, whilst the pure substance actually gives $[\alpha]_D = +26.89^\circ$.

EXPERIMENTS WITH ACETIC ACID AS SOLVENT.

The acetic acid employed boiled at 118° , and had a melting point of 10.4° , a specimen with higher melting point not being available at the time.

Cryoscopic Determinations with Active and Inactive Methylic Dibenzoylglycerate in Acetic acid Solution.

Molecular weight of methylic dibenzoylglycerate = 328.

Molecular depression for acetic acid = 39.

Weight of acetic acid in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point in $^\circ\text{C}$.	Indicated molecular weight.
(a). <i>Active Compound.</i>				
3.7355	0.0785	2.0	0.250	327.9
5.0224	0.1806	3.4	0.460	304.9
3.7500	0.1636	4.1	0.495	343.7*
3.8540	0.2089	5.1	0.690	306.4
5.0565	0.3016	5.6	0.710	327.6
3.7500	0.3197	7.8	0.970	342.9*
4.3326	0.3609	7.7	1.000	324.9
5.0224	0.4212	7.7	1.045	313.0
3.9021	0.3645	8.5	1.080	337.3
3.7500	0.4362	10.4	1.330	341.1*
5.0224	0.6145	10.9	1.515	315.0
3.8540	0.5733	12.9	1.840	315.3
3.9021	0.6024	13.3	1.830	329.0
4.3326	0.6998	13.9	1.850	340.5
5.0224	0.9775	16.2	2.345	323.7

* It will be observed that these figures, which are the most erratic, were all

(b). *Inactive Compound.*

4.4101	0.1145	2.5	0.300	337.5
"	0.2725	5.8	0.770	312.9
"	0.3947	8.2	1.095	318.8
"	0.5317	10.7	1.385	339.5
"	0.6862	13.4	1.750	346.8

From the above figures, it will be seen that the results were of a more erratic character than with the other solvents, the values for the molecular weight being sometimes above and sometimes below the theoretical. This is doubtless to be accounted for partly by the molecular depression possessed by acetic acid being smaller than that of the other solvents, and partly to the very hygroscopic character of the glacial acid, both circumstances which would tend to diminish the accuracy of the determinations. Another circumstance which must have interfered with the accuracy of the results was that the quantities of both solvent and substance employed were exceptionally small.

In the case of the inactive compound, again, the cryoscopic determinations negative the existence of a double molecule racemate in the solution, the values obtained for the molecular weight being essentially similar to those obtained for the active compound.

Solutions of active methylic dibenzoylglycerate were also examined polarimetrically, with the following results.

Rotation of Acetic acid Solutions of Active Methylic Dibenzoylglycerate.

$[\alpha]_D$ for methylic dibenzoylglycerate in state of fusion at $15^\circ \text{C.} = +26.89^\circ$.

Weight of acetic acid solution in grams.	Weight of substance in grams.	Grams of substance in 100 grams of solution.	Observed rotation, α_D , in 100.47 mm. tube.	Density of solution at temperature of observation compared with water at 4° .	Temperature at which rotation was observed.	$[\alpha]_D$
7.6560	0.1313	1.7	+0.63°	1.0561	16.2°	34.34°
5.0756	0.2430	4.7	1.71	1.0694	16.7	32.27
5.8478	0.5548	9.5	3.31	1.0699	15.6	32.45*
7.6152	1.0356	13.6	4.79	1.0750	16.8	32.61
6.0307	1.1219	18.6	6.55	1.0820	16.3	32.38*

obtained in a single series of experiments in which successive additions of the substance were made to *one and the same quantity* (viz., 3.75 grams) of the solvent.

* These solutions were prepared 18 hours before polarimetric examination.

The figures obtained for $[\alpha]_D$ are all in excess of that obtained for the pure substance in a state of fusion at 15° , but they change comparatively little on varying the degree of concentration; the highest dilutions, however, exhibit the greatest rotation, and by reference to the diagram on p. 140 it will be seen that the acetic acid solution gives values for $[\alpha]_D$, which approximate more closely than in the case of the other solvents to the value obtained for the pure substance. On extrapolation for infinite concentration, moreover, it is found that the value for $[\alpha]_D$ almost exactly coincides with the value obtained for the pure substance. Thus on producing the acetic acid straight line beyond the diagram, the value $[\alpha]_D = +27.2^\circ$ is obtained for 100 per cent. concentration, the pure substance giving $[\alpha]_D = +26.89^\circ$ at 15° .

EXPERIMENTS MADE WITH SOLUTIONS OF ACTIVE ETHYLIC DIACETYL-GLYCERATE.

The striking contrasts between the results, both cryoscopic and polarimetric, obtained with benzene and acetic acid solutions of active methylic dibenzoylglycerate, rendered it desirable to ascertain whether similar results would be yielded in the case of other active substances. To this end, cryoscopic and polarimetric determinations were made with benzene and acetic acid solutions of active ethylic diacetylglycerate. The preparation and properties of this compound have already been described by one of us (Percy Frankland and Macgregor, *Trans.*, 1893, **63**, 1422), and the following results were now obtained with its solutions in benzene and acetic acid respectively.

Cryoscopic Determinations with Benzene Solutions of Active Ethylic Diacetylglycerate.

Molecular weight of ethylic diacetylglycerate = 218.

Molecular depression for benzene = 49.

Weight of benzene in grams.	Weight of ethylic diacetylglycerate in grams.	Grams of substance in 100 grams of solution.	Depression of freezing-point in $^\circ\text{C}$.	Indicated molecular weight.
3.5666	0.1261	3.4	0.830°	208.7
"	0.3709	9.4	2.380	214.1
"	0.5208	12.7	3.320	215.5
"	0.6451	15.2	4.050	218.8
"	0.7223	16.8	4.410	225.0
"	0.7988	18.3	4.855	226.1

The above figures show that the solutions of ethylic diacetyl-glycerate in benzene give nearly true cryoscopic values for the molecular weight. The values for the higher dilutions are somewhat below the theoretical, whilst with increasing concentration they rise somewhat above it. The rotation of these benzene solutions was now investigated.

Rotation of Benzene Solutions of Active Ethylic Diacetyl-glycerate.

$[\alpha]_D$ for pure ethylic diacetyl-glycerate at $15^\circ = -16.31$.

Weight of benzene solution, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams of solution.	Observed rotation, α_D , in 100.47 mm. tube.	Density at temperature of observation compared with water at 4° .	Temperature at which rotation was observed.	$[\alpha]_D$.
4.0621	0.2153	5.3	-0.82°	0.8948	15.3°	-17.20°
7.4943	2.2290	29.8	-4.24	0.9580	15.0	-14.83^*

Thus with a low concentration the value for $[\alpha]_D$ is somewhat greater than that exhibited by the pure substance, whilst with a high concentration it is somewhat below the latter.

Similar experiments were then made with solutions of ethylic diacetyl-glycerate in acetic acid.

Cryoscopic Determinations with Acetic acid Solutions of Active Ethylic Diacetyl-glycerate.

Molecular weight of ethylic diacetyl-glycerate = 218.

Molecular depression of acetic acid = 39.

Weight of acetic acid, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams of solution.	Depression of freezing point, in $^\circ\text{C}$.	Indicated molecular weight.
4.8301	0.0521	1.0	0.310	135.7
"	0.1208	2.4	0.705	138.3
"	0.2337	4.5	1.270	148.6
"	0.4678	8.8	2.040	185.2
"	0.7709	13.7	3.250	191.6
"	0.9257	16.1	3.860	193.6

The results present a striking contrast to those obtained in the case of benzene, for with all the concentrations investigated the values

* This solution stood for 18 hours before it was examined.

for the molecular weight were greatly below the theoretical, the values rising with the concentration. Thus whilst with benzene for a concentration of 15·2 per cent. the cryoscopic value for the molecular weight was normal, with acetic acid for a concentration of 16·1 per cent. the value for the molecular weight was much lower than with a concentration of only 3·4 per cent. in the case of the benzene.

Rotation of Acetic acid Solutions of Active Ethylic Diacetyl-glycerate.

$[\alpha]_D$ for pure ethylic diacetyl-glycerate at $15^\circ = -16\cdot31$.

Weight of acetic acid solution, in grams.	Weight of ethylic diacetyl-glycerate, in grams.	Grams of substance in 100 grams solution.	Observed rotation, α_D , in 100·47 mm. tube.	Density at temperature of observation compared with water at 4° .	Temperature of observation of rotation.	$[\alpha]_D$.
4·8922	0·1651	3·4	-1·03°	1·0599	15·1°	-28·74°
9·4825	2·3775	25·0	-5·28	1·0783	15·4	-19·44*

Thus, with a concentration of 3·4 per cent., the value for $[\alpha]_D$ is much greater, and, even with a concentration of 25 per cent., considerably greater than that exhibited by the pure substance.

These results are of particular interest, as showing that even in the case of two compounds so closely allied as methylic dibenzoylglycerate and ethylic diacetyl-glycerate, there may be this great divergence in the optical and cryoscopic properties, according to the solvent employed.

The experimental results recorded in the previous pages may be thus summarised:—

1. Cryoscopic determinations show that inactive methylic dibenzoylglycerate does not exist as a racemised molecule when dissolved in benzene, ethylene dibromide, nitrobenzene, or acetic acid respectively. The values for the molecular weight are in all cases similar to those obtained under the same conditions for that of active methylic dibenzoylglycerate.

2. The cryoscopic values for the molecular weight of methylic dibenzoylglycerate vary according to the solvent and the concentration employed. With benzene, all the values are below the theoretical. With ethylene dibromide and with nitrobenzene, the values are with low concentration below, and with high concentration above the theoretical. In the case of acetic acid, the values are, with all concentrations, sometimes above and sometimes below the theoretical.

3. In all cases, the specific rotation $[\alpha]_D$ of active methylic di-

* This solution stood for 18 hours before examination.

benzoylglycerate is more or less affected by the solvent. In the case of benzene, the values of $[\alpha]_D$ are much in excess, and in that of ethylene dibromide and nitrobenzene they are much below the value of $[\alpha]_D$ for the pure substance. In the case of acetic acid, the values for $[\alpha]_D$ most closely approximate to that of the pure substance.

4. Low cryoscopic values for the molecular weight of methylic dibenzoylglycerate are accompanied by high values for the specific rotation, and *vice versa*.

5. This relationship between specific rotation and indicated molecular weight is borne out by the behaviour of ethylic diacetylglycerate in benzene and acetic acid respectively, but in this case the low molecular weights and high rotations are obtained in acetic acid, the high molecular weight and low rotations in benzene.

6. The real rotation of the active compound cannot be directly calculated from the rotation of its solution, even when the cryoscopic examination of that solution shows the molecular weight to be normal. Thus for methylic dibenzoylglycerate in acetic acid solutions giving normal molecular weights, $[\alpha]_D$ was too high, whilst conversely in nitrobenzene and ethylene dibromide solutions, giving normal molecular weights, the values of $[\alpha]_D$ were too low. By graphic extrapolation for infinite concentration, as in the diagram on p. 140, however, all three solvents give values at any rate approximating to the actual specific rotation obtained with the pure substance. In the case of benzene, on the other hand, all the solutions examined gave molecular weights below the theoretical, and the produced rotation curve gives a value for $[\alpha]_D$ at infinite concentration which departs more widely from the real value than do the produced curves for nitrobenzene, ethylene dibromide, and acetic acid. It would appear, therefore, that even a moderately accurate estimate of the real rotation can only be arrived at by the study of solutions giving normal molecular weights, and extrapolating for infinite concentration on their rotation curves.

Thus the real specific rotation of methylic dibenzoylglycerate is

$$[\alpha]_D = +26.89^\circ \text{ at } 15^\circ \text{ C.,}$$

whilst

$[\alpha]_D$ calculated by extrapolation from benzene solution values.....	= +33.3°
„ calculated by extrapolation from acetic acid solution values.....	= +27.2
„ calculated by extrapolation from nitrobenzene solution values	= +25.0
„ calculated by extrapolation from ethylene dibromide solution values.....	= +32.0
„ calculated from mean of the above extrapolation values.....	= +29.4

7. Our experiments show that the rotation of an active substance may be either raised or depressed by solvents; similarly, the molecular weight, cryoscopically measured, may be either raised or depressed by solvents, the variations in the rotation being doubtless dependent on the variations in molecular weight. Now, the variations in molecular weight can be most consistently explained on the assumption of dissociation and association processes taking place, both of which may go on concurrently.

The phenomenon of dissociation is most conspicuously exhibited in the case of the benzene solution of methylic dibenzoylglycerate and in that of the acetic acid solution of ethylic diacetylglycerate. In both cases, the cryoscopic values for the molecular weight are markedly below the theoretical figures. The effect of this assumed dissociation is in both cases to greatly increase the rotation. The active ion must, however, be different in the two cases, as the dibenzoylglycerate is dextrorotatory, whilst the diacetylglycerate is lævorotatory, although both are derived from one and the same active glyceric acid (dextro-). By dissociation of the dibenzoylglycerate, the rotation becomes more dextrorotatory, whilst by dissociation of the diacetylglycerate the rotation becomes more lævorotatory.

It must not be supposed, however, that the effect of dissociation is invariably to increase the rotation; thus, in Freundler's experiments on the tetra-substituted tartrates, the dissociation was accompanied by diminution in the value of $[\alpha]_D$, thus

	Molecular weight (theoretical).	Molecular weight (cryoscopic).	$[\alpha]$ from benzene solution.	$[\alpha]_D$ real.
Propylic diacetyl- tartrate	318	277	+1.2°.	+13.4°

(*Loc. cit.*, p. 114).

If, in the case of methylic dibenzoylglycerate, high values for specific rotation are shown by cryoscopic measurement to be accompanied by dissociation, we should naturally infer that low values for $[\alpha]_D$ must be due to the opposing influence of association.*

Such low values for $[\alpha]_D$ we find in the case of the ethylene dibromide and nitrobenzene solutions of methylic dibenzoylglycerate. The variation in $[\alpha]_D$ for differences of concentration is comparatively small in the case of these two solvents, but such as it is, this

* Just as there is at present no *à priori* means of ascertaining whether dissociation will be attended by increase or by decrease in the value of $[\alpha]_D$, so there is none for predicting the effect on $[\alpha]_D$ of association.

variation takes place in the opposite sense to that which goes on in the dissociating benzene solution, for with high dilution in the case of ethylene dibromide and nitrobenzene there is a diminution in the values for $[\alpha]_D$ (see the diagram on p. 140). These low values for the specific rotation would thus find the readiest explanation on the hypothesis of association becoming more pronounced the greater the dilution of the solution.

Of such association at high dilutions there is, however, no direct evidence from the cryoscopic determinations, the indicated molecular weights in the case of ethylene dibromide, and still more so in the case of nitrobenzene being somewhat below the theoretical value. On the other hand, with these two solvents at high concentrations, the indicated values for molecular weight are considerably in excess of the theoretical. But if these high indicated molecular weights were the result of association we ought to find the values for $[\alpha]_D$ simultaneously falling, whilst, as a matter of fact, they rise with the concentration.

The only polarimetric confirmation of this cryoscopic evidence of association which we can find in our experiments is in the case of the benzene solutions of ethylic diacetylglycerate. Here the most concentrated solutions give indicated molecular weights in excess of the theoretical, the value of $[\alpha]_D$ calculated from such solutions being less than the value of $[\alpha]_D$ for the pure substance, and since the dilute solutions give cryoscopic evidence of dissociation accompanied by excessive values for $[\alpha]_D$, we can conclude that association and deficient values for $[\alpha]_D$ are connected, and that the deficient value for $[\alpha]_D$ with high concentration is confirmation of the association cryoscopically indicated.

Amongst the experimental material furnished by Freundler (*loc. cit.*, p. 117) there are the following cases exhibiting cryoscopic evidence of association.

Benzene Solutions.

Active compound.	Molecular weight (theoretical).	Molecular weight (found).	$[\alpha]_D$ measured on the solution.	$[\alpha]_D$ obtained with the pure substance.
Methylic tartrate. . .	178	411	-8.8°	+2.14°
Propylic ,, . . .	234	306	+20.1	+12.44

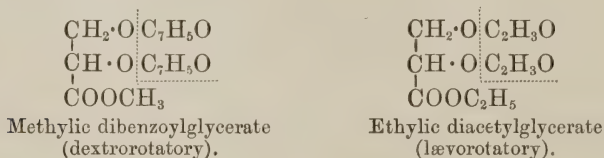
Ethylene Dibromide Solution.

Propylic tartrate. . .	234	326	-0.6°	+12.44°
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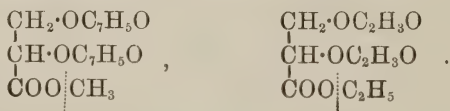
Thus, in all the above cases, the cryoscopic determinations afford

strong evidence of association, and yet the effect on the rotation is quite irregular, for in the benzene solution the effect on the rotation of methylic tartrate is negative, whilst in that of propylic tartrate it is positive. There is of course nothing surprising in these results, as association with the molecules of the same solvent may produce opposite rotatory effects in the case of two different active compounds, and association with the molecules of two different solvents may produce opposite rotatory effects in the case of one and the same active compound.

In his experiments on the tetra-substituted tartrates, Freundler finds evidence, in several cases, of dissociation in organic solvents, and is of opinion that the dissociation consists in the splitting off of the two acid radicles* substituting the two alcoholic hydrogen atoms of the tartaric acid. Our experiments, however, clearly show that the molecules of the fully substituted glycerates dissociate otherwise. Thus, as already pointed out, methylic dibenzoylglycerate dissociates in benzene, and the active ion is more dextro-rotatory than the undissociated molecule. Ethylic diacetylglycerate, on the other hand, dissociates in acetic acid, and the active ion is more powerfully lævorotatory than the undissociated compound. Thus, the two active ions differ not only in sign but enormously in degree, whilst, if the acid radicles were split off, the only difference in their constitution would be the presence of methyl in the one and of ethyl in the other, thus

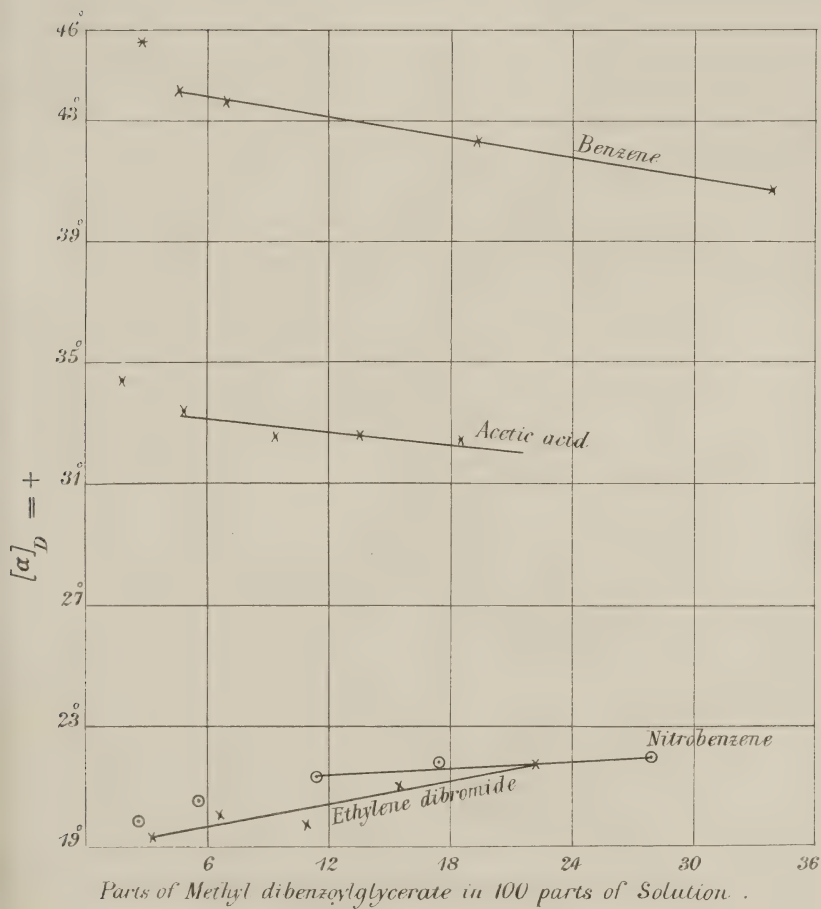


But we know that the dextrorotation of the dibenzoylglycerates is conditioned by the benzoyl groups, and the methylglyceryl and ethylglyceryl ions could not possibly differ in rotation to the extent which the ions in question actually do, hence we regard the dissociation as almost certainly taking place as indicated below.



* This supposition is quite out of harmony with Perkin's experiments on diethylic benzoyltartrate, in which it was found that by hydrolising with an insufficient quantity of alcoholic potash benzoyltartaric acid was formed, the ethyl groups being eliminated, whilst the benzoyl groups remained attached (Trans., 1867, 20, 141).

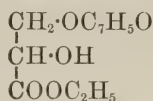
SPECIFIC ROTATION OF METHYL DIBENZOYLGLYCERATE IN VARIOUS SOLVENTS
(BENZENE, ACETIC ACID, NITROBENZENE AND ETHYLENE DIBROMIDE.)



○ Nitrobenzene.

This process would leave the active ions differing profoundly in constitution as they do in rotation.

We have recently obtained further evidence bearing on this point, in connection with the rotation of ethylic monobenzoylglycerate. This substance which has been prepared by one of us in conjunction with Mr. MacGregor is in all probability the β -compound, of the formula



In a state of fusion, the specific rotation of this substance is $[\alpha]_{\text{D}} = -9.80^\circ$, whilst, with a benzene solution, the following result was obtained.

Weight of benzene solution, grams.	Weight of substance in grams.	Grams of substance in 100 grams solution.	Observed rotation α_{D} in 198.4 mm. tube.	Density of solution compared with water at same temperature.	Temp. of observation of rotation.	$[\alpha]_{\text{D}}$.
9.5558	1.3701	14.3	-0.925°	0.9194	15.5°	-3.5°

Thus the activity of the substance in benzene solution was far less lævorotatory than in the pure state, a circumstance which is quite in harmony with the supposition that in benzene solution the molecule is more or less dissociated into a C_2H_5 -ion and the complex active ion $\text{C}_{10}\text{H}_9\text{O}_5$. For, as already pointed out, in these ethereal salts of glyceric acid, dextrorotation is conditioned by the presence of benzoyl groups in place of the hydroxylic hydrogen atoms; whilst lævorotation is conditioned by the positive radicles replacing the carboxylic hydrogen; now if, in the above substance the benzoyl group were split off in the dissociation supposed to take place in the benzene solution, then the molecule should become more lævorotatory; on the other hand, if it is the ethyl group that is split off we should anticipate that the molecule would become more dextrorotatory by virtue of the more preponderating influence obtained by the benzoyl group; and this is precisely what takes place, for in benzene solution the substance actually becomes more dextrorotatory, or rather its lævorotation is greatly diminished.

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XV.—*The Molecular Volumes of Organic Substances in Solution.*

By W. W. J. NICOL, M.A., D.Sc., F.I.C.

THE sixth report of the Committee on Solution presented to the meeting of the Chemical Section of the British Association in Edinburgh in 1892, contained a short notice of some preliminary experiments on this subject.

My attention was first directed to this question in 1883, when I was the first to show that in the case of salts in dilute aqueous solution, the difference between the molecular volumes of the salts of any two metals is a constant, irrespective of the salt radicles with which the metals are combined, and that the same holds good with regard to any two salt radicles. In the course of the experiments necessary to establish this law, I had occasion to determine the molecular volumes of the sodium and potassium salts of formic, acetic, and butyric acids, and found that an increase of CH_2 in the molecular weight was attended by an increase in the molecular volume of approximately 14.3 (*Phil. Mag.*, 1883, **16**, 131). At the conclusion of the paper, I pointed out that "this method of investigating the molecular volumes of salts is, in all probability, capable of extension to organic substances, and that, by comparing solutions of various organic bodies which differ by one or more CH_2 groups, or in other respects, it may be possible to determine the volume of these differences. Such solutions need not necessarily be aqueous."

In the Report above referred to (*Brit. Assoc. Reports*, 1892, 261), the following passage occurs: "This point appeared worthy of further examination, inasmuch as, if dissolved substances are under comparable conditions when the solution is sufficiently dilute, as seems most probable from a consideration of the physical properties of such solutions, then the apparent molecular volumes in dilute solution could be compared in the same way as the molecular volumes at the boiling point, and thus the atomic volumes of the various elements could be determined with greater ease and certainty than at the boiling point."

The present communication relates to the increase in molecular volume in dilute solution, produced by the successive additions of the group CH_2 , in the ethereal salts, and partakes largely of the nature of a preliminary note: the appearance of some recent communications on the same and closely allied subjects rendering it necessary that I should place on record the work that I have already done.

The method of investigation is as follows:—Fifty c.c. of the

solvent is weighed to the nearest milligram, and 2 c.c. of the ethereal salt in question is added and again weighed to the nearest milligram. The specific gravity of the solution, the composition of which is thus known, is determined in duplicate, by means of capped Sprengel tubes immersed in a constant temperature bath at 20°, the variation of the temperature of which does not exceed $\pm 0.01^\circ$. The accuracy of the specific gravity determinations is shown by the fact that the mean difference between any two duplicate determinations does not exceed 0.000017. From the composition of the solutions and their specific gravities, their molecular volumes are calculated in the usual way, and the molecular volume of the solvent being known, the differences are the apparent molecular volumes of the dissolved salts.

The ethereal salts were obtained from Schuchardt, and, as far as the quantity at my disposal permitted, were fractionated, that fraction being used which most closely agreed with the generally accepted boiling point: there is, however, every reason to believe that the small differences observed below are due, in many cases, to impurities present in these salts.

Table I contains the experimental results; it has not been considered necessary to tabulate the composition and specific gravity of

TABLE I.—*Molecular Volumes of Ethereal Salts in different Solvents.*

Ethereal salt.	Molecular weight.	Xylene.	Benzene.	88 per cent. alcohol.
Methylic acetate	74	80.2	80.4	80.1
Ethylic formate.....	74	81.1	82.0	81.1
Amylic formate.....	116	131.4	133.3	133.3
Butylic acetate*.....	116	131.9	134.0	134.3
Ethylic butyrate†....	116	131.5	132.3	132.8
„ oxalate.....	146	136.0†	135.6	136.0
„ benzoate.....	150	142.4	142.7	143.0
„ salicylate	166	147.8	148.3	147.2
„ malonate*....	160	—	151.6	153.5
„ valerate.....	130	149.4	150.1	150.6
Amylic acetate.....	130	149.5	150.8	150.7
Ethylic succinate.....	174	167.0	166.2	168.0
Amylic benzoate	192	191.5	192.1	192.9
„ valerate.....	172	200.3	201.5	203.1

Water at 20° C = 1, the above = c.c. per gram-molecule.

each solution, but only the molecular volumes of the ethereal salts in the three solvents, xylene, benzene, and 88 per cent. alcohol, on the supposition that the volume of the solvent remains constant.

* Of doubtful purity.

† 1 c.c. to 50 c.c. xylene.

‡ 1 c.c. to 50 c.c. xylene.

In Table II, the results for isomers are collected together; as the result of this comparison, it is seen that methylic acetate has a considerably smaller volume than ethylic formate, a point already observed in the case of their molecular volumes at the boiling point, and in accordance with the general law observed by Elsässer (*Annalen*, 1883, **218**, 302) at the ordinary temperature, and by Schiff (*ibid.*, 1883, **220**, 325) at the boiling point, that in the case of isomeric salts, the one with the smaller acid radicle has the greater volume. That the other isomeric ethereal salts in Table II do not show this clearly is probably due to their not being the normal compounds. If a comparison be made of the mean values for each set of isomers, we find that the first addition of 3CH_2 is attended by a greater increase of volume than the second, which is not observed in the boiling point determinations.

TABLE II.—*Molecular Volumes of Isomeric Ethereal Salts in different Solvents.*

Ethereal salt.	Xylene.	Benzene.	88 per cent. alcohol.
Methylic acetate	80·2	80·4	80·1
Ethylic formate	81·1	82·0	81·1
Mean.....	80·7	81·2	80·6
Amylic formate.....	131·4	133·3	133·3
Butylic formate.....	131·9	134·0	134·3
Ethylic butyrate	131·5	132·3	132·8
Mean	131·6	133·2	133·4
Ethylic valerate.....	149·4	150·1	150·6
Amylic acetate.....	149·5	150·8	150·7
Mean.....	149·5	150·5	150·7
Increase for first 3CH_2	50·9	52·0	52·8
„ for second 3CH_2	47·9	47·3	47·3
Mean value of CH_2	16·5	16·6	16·7

In Table III are given the mean values of CH_2 as obtained from a comparison of the homologous compounds, and the final mean may be taken as the approximate volumes of CH_2 in the three solvents.

Further, Table I contains data relating to four ethereal salts not taken into account in the above comparison. Ethylic oxalate, malonate, and succinate differ respectively by CH_2 , comparing the first and last, $2\text{CH}_2 = 31·0, 30·6, 32·0$, in the three solvents, a volume much smaller

TABLE III.—*Mean value of CH₂ from a Comparison of*

Ethereal salts.	Xylene.	Benzene.	88 per cent. alcohol.
Formates	16·8	17·1	17·4
Acetates	17·3	17·6	17·6
Valerates	17·0	17·1	17·5
Benzoates	16·4	17·1	17·5
Isomers	16·5	16·6	16·7
Mean.....	16·8	17·0	17·3

than that found above; the cause of this may lie in contraction, brought about by the separation of the carboxyl groups, for it is evident that the introduction of CH₂ here, is not comparable with the passage from the methyl to the ethyl group. This point requires further investigation. A comparison of the volumes of ethylic benzoate and salicylate gives the value of the group OH = 5·4, 5·6, 4·2.

The important question as to the reason of the differences observed between the volumes of the same substance in the three solvents must be left over until the effect of dilution on the molecular volume has been fully examined in the case of solvents of widely different molecular weight: it is, I believe, closely connected with the question of the aggregation of molecules in solution; the solvent with the heavier molecules, xylene, breaking down these aggregations more completely, brings about a diminution of the molecular volume.

XVI.—*Action of Sugars on Ammoniacal Silver Nitrate.*

By JAMES HENDERSON, B.Sc., 1851 Exhibition Scholar, University College, Dundee.

WHILE recently pursuing a research in which it was essential that very small quantities of sugars produced in the course of experiment should be estimated quickly and accurately, and as the requirements were such as to preclude the adoption of any of the various copper-reducing methods, the author was led to undertake this research, with the view of discovering a method whereby such an estimation could be satisfactorily accomplished. The principle of the method adopted in this case, like Fehling's, is based on the fact that alkaline solutions of certain metals undergo reduction when heated with certain oxidisable compounds, such, for example, as sugars. Tollens

(*Ber.*, 1883, **16**, 921) has shown that when dextrose is heated with ammoniacal silver nitrate, the number of atoms of silver reduced for each molecule of dextrose varies according as a greater or smaller excess of the silver solution is employed, as shown in the following results which he obtained.

Silver taken.	Silver reduced.	Ratio of 1 mol. of dextrose to atoms of silver.
104.3	102.44	12.29
115.6	108.00	12.96
176.8*	147.39	17.69

The quantity of silver nitrate originally taken was thus only slightly in excess of that used up by the dextrose. Experiments conducted under the above conditions cannot be expected to yield very constant results, as the amount of silver nitrate employed in each case is evidently insufficient to ensure the complete oxidation of the sugar to some definite final stage; it appeared to me, however, that this could be readily effected by heating the dextrose for a sufficient length of time with a fairly large excess of silver nitrate. Preliminary experiments were accordingly made with a view to determine what influence, if any, time, and the presence of a larger or smaller quantity of ammonia exerted on the reduction of the silver nitrate by the sugar. A solution of ammonia of sp. gr. = 0.88, diluted with three times its own volume of water, was added to a given volume of decinormal solution of silver nitrate until the precipitated oxide was just redissolved; a known volume of a standard solution of dextrose was then added, and the mixed solutions introduced into a boiling tube, and heated by means of steam issuing freely from a small copper boiler, into the neck of which the boiling tube was slipped, the greater part of the tube being thus subjected to the action of the vapour. After heating the solution at 100° for a definite time, a known volume was taken out by means of a pipette, cooled, diluted with water, and the reduced silver collected on a filter, and thoroughly washed with distilled water; the mixed filtrate and washings were then acidified with strong nitric acid, and titrated with N/50 ammonium thiocyanate, iron alum being used as an indicator. This strength of ammonium thiocyanate solution was used throughout, except in estimating the reducing powers of cane sugar, dextrin, and starch, where a decinormal solution was employed. This mode of estimating the unreduced silver nitrate was invariably used throughout the whole of the research. The influence of time on the reducing action of the sugar was first of all ascertained in the following manner. A known volume of a standard solution of

* In presence of caustic soda.

dextrose was added to 40 c.c. of decinormal silver nitrate, containing ammonia just sufficient to keep the precipitated oxide in solution, and the mixed solutions heated at 100° in the manner already described. Five c.c. of the solution were taken out at various intervals, and the amount of unreduced silver nitrate estimated.

Dextrose.	Time of heating at 100° C.	Amount of AgNO_3 N/10 reduced.
20 milligrams.	0.33 min.	1.64 c.c.
—	5.0 mins.	1.66 „

This, then, would seem to indicate that with the above ratio of concentration of dextrose to silver, the reducing action of the sugar ceases in about half a minute from the start.

The next experiments were made with the view of ascertaining the influence of ammonia on the reducing power of dextrose. A known volume of a standard solution of dextrose was mixed with 20 c.c. of decinormal silver nitrate containing 5 c.c. of ammonia solution, and the mixture heated at 100° . The same volume of ammonia solution was added in every case, although the strength of the solution varied throughout the series from 1 : 3 to 1 : 7.

Five c.c. were taken out at various intervals, and the excess of silver nitrate estimated as before. The final ratio of silver nitrate reduced to that remaining in the solution was the same in each case, namely, 1 : 2.

Dextrose.	Strength of ammonia solution.	Time of heating.	AgNO_3 N/15 reduced.
10 milligrams	1 : 7	{ 0.33 mins.	1.92 c.c.
		{ 7.25 „	1.64 „
		{ 12.41 „	1.46 „
10 „	1 : 6	{ 0.41 „	1.68 „
		{ 4.00 „	1.44 „
		{ 13.05 „	1.46 „
10 „	1 : 5	{ 0.33 „	1.64 „
		{ 4.75 „	1.53 „
10 „	1 : 4	{ 0.50 „	1.53 „
		{ 7.50 „	1.55 „
10 „	1 : 3	{ 0.70 „	1.50 „
		{ 5.58 „	1.49 „
10 „	1 : 3	{ 5.41 „	1.67 „
		{ 14.58 „	1.52 „
		{ 27.08 „	1.45 „

The results obtained above are sufficient to demonstrate the rather interesting fact that, provided the concentration of silver nitrate to dextrose remains the same throughout the series, the strength of the ammonia solution employed does not appreciably influence the amount

of reduction of the silver nitrate; and further, when the above concentration is adopted, it would appear, from the numbers obtained, that prolonged heating of the solution affects the reducing power of the sugar to a very limited degree. The next series of experiments was undertaken with the object of ascertaining the effect produced by varying the amounts of dextrose, the quantity of silver nitrate taken being the same in each experiment. A known volume of dextrose solution was added to 20 c.c. of decinormal silver nitrate containing 5 c.c. of ammonia solution, made by diluting ammonia, sp. gr. 0·88, with thrice its volume of water. The solution was then heated at 100°, 10 c.c. taken out at intervals, and an estimation made of the unreduced silver nitrate in that volume of solution.

Dextrose.	Time of heating.	AgNO ₃ N/10 reduced.	Ratio of dextrose taken to silver nitrate reduced, expressed in milligrams.
8 milligrams	{ 5·0 mins.	1·84 c.c. }	1 : 3·9
	{ 10·5 "	1·86 "	
6 "	{ 5·0 "	1·46 "	1 : 4·1
	{ 10·5 "	1·46 "	
4 "	{ 5·0 "	1·04 "	1 : 4·2
	{ 10·5 "	0·98 "	

From these results we deduce the fact that, provided the amount of silver nitrate taken is the same in every case, the amount of reduction of the silver nitrate present in the solution is proportional to the amount of dextrose present. From the quantity of silver nitrate reduced by a given volume of a standard solution of dextrose, we are able to calculate the "factor" for ammoniacal silver nitrate, that is, the number of molecules of silver nitrate which are equivalent to 1 mol. of dextrose.

The following series of experiments was undertaken, with the object of ascertaining the true value of this factor.

Dextrose.	AgNO ₃ N/10.	AgNO ₃ (N/10) reduced.	Ratio of silver nitrate reduced to that remaining in solution.	Factor.
10·0 milligrams	30 c.c.	6·65 c.c.	1 : 3·51	11·97
10·0 "	30 "	6·64 "	1 : 3·51	11·95
10·0 "	30 "	6·65 "	1 : 3·51	11·97
7·0 "	30 "	4·60 "	1 : 5·52	11·80
4·0 "	30 "	2·60 "	1 : 10·53	11·70
17·5 "	40 "	11·73 "	1 : 2·42	12·06

Five c.c. of ammonia solution of the same strength as before (1 : 3) were mixed with 30 c.c. of decinormal silver nitrate, and to this was added a definite volume of a standard dextrose solution. After heating at 100° for eight minutes, the whole solution was cooled, diluted, and the reduced silver filtered off, the excess of silver nitrate being estimated in the usual manner. The following results were obtained.

The dextrose used in the above experiments was a pure specimen obtained by recrystallisation from water.

With ordinary commercial glucose, the following results were obtained.

Glucose.	AgNO_3 (N/10).	AgNO_3 (N/10) reduced.	Ratio of silver nitrate reduced to that remaining in solution.	Factor.
17.5 milligrams	30 c.c.	11.7 c.c.	1 : 1.56	12.0
10.0 ,,	30 ,,	6.9 ,,	1 : 3.34	12.4

Taking the mean of the results of the first series, we obtain the factor value 11.9.

Soxhlet (*J. pr. Chem.*, [2], 1880, **21**, 227) has clearly established the fact that in the case of the reduction of Fehling's solution by dextrose the dextrose equivalent has by no means a constant value, but, on the contrary, is entirely dependent on the particular circumstances under which the reduction is effected. The causes chiefly affecting the reduction of the copper solution in the case of dextrose are dilution, concentration of solutions, and the time of heating. As a consequence of this, therefore, when estimating dextrose in different solutions, the results are comparable only when the experiments are conducted under precisely the same conditions of dilution, &c. As has already been shown in the case of the reduction of silver nitrate by dextrose, the influence of time ceases after 5—10 minutes; moreover, it would appear that, provided the solution be heated for a sufficient length of time, namely, 8—10 minutes, and provided also that the ratio of concentration of the reduced silver to the silver left in the solution does not fall below 1 : 2, the amount of reduction of the silver nitrate is dependent solely on the quantity of reducing sugar present in solution. This at once suggests a method for the quantitative estimation of dextrose in dilute solutions.

A series of estimations was next performed for the purpose of testing the accuracy of the value obtained for the dextrose factor.

2.5 c.c. ammonia solution of the usual strength (1 : 3) were added to 10 c.c. of decinormal silver nitrate, a known volume of standard dextrose solution was then added, and the solution heated at 100° for

eight minutes. The reduced silver was next filtered off, and the excess of silver nitrate determined by titration. The factor used was that obtained in the previous experiments, namely 11.9.

Dextrose.		Ratio of silver nitrate used to that remaining in solution.	AgNO ₃ (N/10) reduced.
Milligram taken.	Milligram found.		
5.0	5.0	1 : 3.07	3.32 c.c.
5.0	4.9	1 : 3.2	3.25 "
10.0	9.4	1 : 1.59	6.23 "

Evidently, therefore, with a ratio varying from 1 : 2 to 1 : 3 fairly accurate results can be obtained.

Cane Sugar.

A pure specimen of cane sugar was prepared by recrystallisation from ethylic alcohol. A known volume of a standard solution of the pure sugar was heated at 100° for a certain length of time with 20 c.c. of decinormal silver nitrate and 5 c.c. of ammonia solution (1 : 3); at the conclusion, the solution remained perfectly clear, exhibiting no signs of reduction of the silver nitrate, subsequent titration of the whole solution proving that no action had taken place.

Cane sugar.	AgNO ₃ (N/10).	Time of heating.	AgNO (N/10) reduced.
160 milligrams	20 c.c.	10 mins.	—
20 "	20 "	25 "	—

A dilute solution of cane sugar is therefore incapable of effecting the reduction of ammoniacal silver nitrate when the above concentration is used, but if stronger solutions of the sugar are used, and more especially if the mixed solutions are heated for a longer period, the cane sugar begins to be slowly oxidised at the expense of the silver nitrate; this in all probability is due to the slow hydrolysis of the disaccharide molecules by the alkali, sugars being formed which of course are capable of being oxidised by silver nitrate. This secondary action is even more marked in the case of Fehling's solution; at first no signs of reduction are observable, but, on continued boiling, they very soon begin to manifest themselves. This inability on the part of the silver solution to effect the oxidation of the cane sugar may be utilised as the basis of a method for the estimation of dextrose in presence of cane sugar.

2.04 grams of dextrose and 4.063 grams of cane sugar were dissolved in water, and the solution made up to a litre. A given volume of this solution was then heated at 100° with a known volume of decinormal silver nitrate and 2.5 c.c. of ammonia solution (1 : 3) for a certain time, the reduced silver filtered off, and the excess of silver nitrate determined in the usual way.

Dextrose.		$\text{AgNO}_3(\text{N}/10)$.	$\text{AgNO}_3(\text{N}/10)$ reduced.	Time.	Ratio of silver nitrate reduced to that left in solution.
Milligrams taken.	Milligrams found.				
10.2	7.25	10 c.c.	4.85 c.c.	8 mins.	1 : 1.06
5.1	4.72	10 "	3.15 "	12 "	1 : 2.1
5.1	4.87	10 "	3.25 "	18 "	1 : 2.1
5.1	4.95	10 "	3.30 "	23 "	1 : 2.03
5.1	5.1	20 "	3.40 "	8 "	1 : 4.8

The presence of cane sugar in the solution appears to retard the oxidising action of the silver nitrate to a slight extent. A quantity of silver nitrate sufficient to oxidise a known amount of dextrose to a certain stage in a given time is incapable of doing so in presence of cane sugar in the same time; this retarding action may be remedied either by increasing the time of heating, or perhaps better by increasing the amount of silver nitrate.

Dextrin and Starch.

A specimen of ordinary dextrin was purified by dissolving it in water, filtering, and precipitating with 90 per cent. alcohol; the precipitate was then washed with strong alcohol and dried in a vacuum desiccator. The reducing power of each substance was then estimated by heating a definite volume of the standard carbohydrate solution for eight minutes at 100° with 10 c.c. of decinormal silver nitrate and 2.5 c.c. of ammonia solution (1 : 3).

	$\text{AgNO}_3(\text{N}/10)$.	$\text{AgNO}_3(\text{N}/10)$ reduced.
Dextrin: 16.2 milligrams	10 c.c.	—
Starch: 4.05 " "	10 "	—

Hence dilute solutions of dextrin and starch, like cane sugar, do not reduce ammoniacal silver nitrate. Reducing sugars can be estimated, therefore, in presence of either or both of these compounds.

Schering's Levulose.

The method used in determining the reducing power of this sugar was identically the same as that adopted in the case of dextrose.

Levulose.	AgNO ₃ (N/10).	AgNO ₃ (N/10) reduced.	Time of heating.	Ratio of silver nitrate reduced to that left in solution.	Factor.
10 milligrams	30 c.c.	5.38 c.c.	8 mins.	1 : 4.57	9.7
10 "	30 "	5.38 "	15 "	1 : 4.57	9.7
10 "	40 "	5.57 "	8 "	1 : 6.17	10.0
10 "	60 "	5.80 "	8 "	1 : 9.34	10.4

As with dextrose, the reducing power of levulose is but slightly influenced by the time of heating after eight minutes.

Galactose.

A pure specimen was obtained by recrystallisation from ethylic alcohol. A standard solution of the pure sugar was then prepared, and a given volume heated at 100° with 30 c.c. of decinormal silver nitrate and 5 c.c. of ammonia solution (1:3). After a certain interval, the reduced silver was filtered off and the excess of silver in the solution estimated as usual. The results of these experiments were as follows.

Galactose.	AgNO ₃ (N/10) reduced.	Time of heating.	Ratio of silver nitrate reduced to that left in solution.	Factor.
10.0 milligrams	6.73 c.c.	8 mins.	1 : 3.4	12.11
10.0 "	6.70 "	12 "	1 : 3.4	12.07
7.0 "	4.70 "	8 "	1 : 5.37	12.08

Factor = 12.08 (mean).

As in the case of dextrose and levulose, time exerts little or no influence on the reducing power of galactose after eight minutes' heating at 100°. It will be observed that the mean of the values obtained for the factor is almost equal to that of dextrose (11.9).

Lactose.

The sugar used in these experiments was obtained by recrystallisation from aqueous alcohol. A standard solution of this pure sugar was prepared and its reducing power estimated as in the previous cases.

Lactose.	AgNO ₃ (N/10).	AgNO ₃ (N/10) reduced.	Time.	Ratio of silver nitrate reduced to that left in solution.	Factor calculated for C ₁₂ .
10 milligrams	40 c.c.	2.70 c.c.	8 mins.	1 : 13.80	9.72
10 "	40 "	4.19 "	16 "	1 : 8.54	14.76
10 "	40 "	4.60 "	20 "	1 : 7.69	16.56
10 "	40 "	5.30 "	25 "	1 : 6.54	19.08
10 "	40 "	6.75 "	30 "	1 : 4.92	24.30

Maltose.

The specimen of maltose used in these experiments was prepared in the following way. A saturated solution of the sugar in alcohol was allowed to remain for more than a fortnight in a corked flask; the solution was then filtered from the maltose which had separated, and the alcohol allowed to evaporate slowly in the air. A standard solution of the sugar thus obtained was then prepared, and the reducing power estimated in the usual manner.

Maltose.	AgNO ₃ (N/10).	AgNO ₃ (N/10) required.	Time.	Ratio of silver nitrate reduced to that left in solution.	Factor calculated for C ₁₂ .
10 milligrams	20 c.c.	0.95 c.c.	8 mins.	1 : 20.05	3.40
10 "	20 "	1.07 "	8 "	1 : 17.6	3.85
10 "	20 "	1.27 "	15 "	1 : 14.69	4.57
10 "	40 "	7.25 "	30 "	1 : 4.5	26.10

Hence when either lactose or maltose is heated with ammoniacal silver nitrate under conditions sufficient to oxidise the same amount of any of the monosaccharides, dextrose, galactose, or levulose, to a definite final stage, only a very small proportion of the disaccharide becomes oxidised. The results of the time experiments in the case of lactose and maltose would lead us to suspect a gradual hydrolysis of the sugar by the ammonia as the heating is continued.

The results obtained may be thus summarised.

- (1) When dextrose, levulose, and galactose are heated with ammoniacal silver nitrate under the given conditions, a definite factor can be obtained in each case.
- (2) Cane sugar, starch, and dextrin, when heated under the same conditions, exert no reducing action on ammoniacal silver nitrate.

- (3) In the case of lactose and maltose a definite factor cannot be got, owing to the gradual hydrolysis of the disaccharide molecules by the ammonia.

University College, Dundee,
December, 1895.

XVII.—*The Molecular Weight and Formula of Phosphoric Anhydride and of Metaphosphoric Acid.*

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Phosphoric Anhydride.

Considerable advances have been made within recent years in the study of compounds of the elements belonging to the phosphorus group, and among the results established may be remarked especially the fact that the oxides generally, and several of the sulphides, conform to the molecular type of the elements themselves, that is, they contain four atoms of phosphorus, arsenic, or antimony. The formulæ, As_4O_6 , and Sb_4O_6 , have been established for arsenious and antimonious oxides respectively by the vapour density determinations published by V. and C. Meyer (*Ber.*, 1879, **12**, 1117, 1282). The formulæ, P_4O_6 , and $\text{P}_4\text{O}_6\text{S}_4$, have in like manner been settled by Thorpe and Tutton (*Trans.*, 1890, **57**, 551, and 1891, **59**, 1022), and the lower sulphide has the corresponding formula, P_4S_6 , calculated from the density of its vapour (*Isambert, C.R.*, 1886, **102**, 1386). The case of the higher sulphide will be discussed later on. The compound described by Thorpe and Tutton under the name of phosphorus tetroxide (*Trans.*, 1886, **49**, 833), is regarded by them as having the molecular formula, P_2O_4 , and hence as the analogue of nitrogen tetroxide, but no determination of the vapour-density has yet been attempted.

Phosphoric anhydride alone remains unexamined among the compounds of phosphorus which are volatile without dissociation, but it is usually still expressed as pentoxide, P_2O_5 , from analogy with the sulphide, the vapour density of which has been determined by V. and C. Meyer (*Ber.*, 1879, **12**, 610).

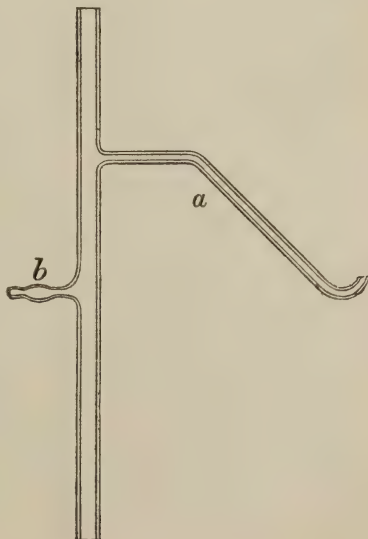
According to Shenstone and Beck (*Trans.*, 1893, **63**, 475), phosphoric anhydride usually contains lower oxides of phosphorus; for the preparation of the pure oxide we have, therefore, adopted their process with slight modifications. The sublimed product, after passing together with dry oxygen through the heated platinum sponge,

was collected in a narrow tube of hard glass united by means of the blowpipe to the end of the combustion tube. When full, this tube was drawn off at its junction with the combustion tube, exhausted by the Sprengel pump and sealed. Separate small portions could then be sealed off for successive experiments.

The oxide thus obtained was chiefly in the form of a crystalline crust adherent to the glass, but also partly in a loosely flocculent condition. When free from phosphoric acid, it does not melt on the application of heat, but sublimes rapidly below a red heat. An attempt was made to melt the oxide in a tube attached to an apparatus in which it could be exposed to a pressure of nearly 7 atmospheres. On applying the flame of a spirit lamp, however, the substance sublimed without melting.

In order to determine the vapour-density of this substance, it is necessary, on account of its extremely hygroscopic nature, to avoid contact with ordinary undried air. Platinum is the only available substance capable of resisting to a sufficient extent its action at a red heat, though even platinum is liable to be corroded, especially in the presence of oxygen (Barnett, Trans., 1895, 67, 513). Hence peculiar difficulties stand in the way of exact determination of the density of the vapour of phosphoric anhydride, and the results of our earlier experiments were unsatisfactory owing to various causes which it is unnecessary to discuss here, being attributable in most cases to insufficiently high temperature, or to some imperfection in the apparatus. It may, however, be stated that the value deduced for the molecular weight was in every case more than double the number, 142, which corresponds to the formula, P_2O_5 .

The method used was Victor Meyer's air expulsion process. The apparatus consisted of a cylindrical platinum bottle, 10 cm. high and 6 cm. in diameter, holding about 300 c.c. and having a tubular neck 40 cm. long by $1\frac{1}{2}$ cm. internal diameter. Into the end of this platinum tube was fitted a glass tube with two branches; one, a narrow bore gas-leading tube, *a*, the other a short straight tube *b*, which could be closed by a stopper. The top of the glass tube was closed by a



rubber stopper traversed by a perforation through which passed, gas-tight, a glass rod having a mark upon it so that it could always be pushed in to the same extent. The small tube containing the substance could be inserted into the rubber stopper from below, and would be held in the perforation until pushed out by the glass rod. The source of heat was in the earlier experiments a gas muffle, but this was afterwards replaced by a gas furnace in which the platinum bottle could stand upright. It was found necessary to protect the platinum from contact with the furnace gases, and accordingly we procured some glazed fireclay cylinders closed at one end, into which the bottle would just slide, and with this covering it was placed in the furnace. The top of the cylinder projecting into the air was packed with asbestos card so as to prevent cooling by convection. The expelled air was at first collected over oil of vitriol, but as this was inconvenient it was replaced by kerosene of known density and vapour-pressure. In order to fill the bottle with dry air, a long tube passed through the rubber stopper to near the bottom of the bottle. As the end of this tube when wholly of glass was found to collapse when hot, about 30 cm. of the lower end was replaced by a tube of platinum foil. Bulbs filled with oil of vitriol and phosphoric anhydride were connected with the side-branch, and thus a current of dried air entered here, passed down into the bottle, and escaped up the long tube. This operation was performed after the platinum bottle had been heated to the requisite temperature and all was ready for the experiment. By making use of the same side-branch and long tube at the end of an experiment, the vapour could be expelled and the apparatus left ready for a second operation.

An approximate estimation of the temperature obtained was made by means of the melting-points of salts. A few crystals of the dry salt were wrapped in a little cylinder of platinum gauze and lowered into the bottle when heated. Suspended at a distance of 2 c.m. from the bottom, sodium chloride was always melted, while potassium sulphate only showed signs of incipient fusion. The latest values for the melting-points of these salts are 815° and 1078° respectively (V. Meyer, Riddle, and Lamb, *Ber.*, 1894, **27**, 3128). It may, therefore, be concluded that the temperature in the later experiments was in the neighbourhood of 1000° .

The little tube containing the phosphoric anhydride having first been nicked by a file near one end, and wrapped in a piece of platinum foil, was weighed. A crack was then started in the tube by the application of a hot rod, the extremity broken off, and the tube instantly fixed in its place. The glass was weighed after the experiment was over and it was always found that the two pieces fitted together perfectly.

The following results were obtained in the manner described.

No.	Weight of phosphoric anhydride.	Vol. of air reduced to 0° and 760 mm.	Vapour density.	Molecular weight.
1	0·2533 gram	15·96 c.c.	177·0	354
2	0·0841 „	5·06 „	185·0	370
3	0·2055 „	14·02 „	163·0	326
4	0·1904 „	13·83 „	153·6	307
5	0·2600 „	18·22 „	163·0	326
6	0·1859 „	12·38 „	167·5	335

Calculated molecular weight, for $P_2O_5 = 142$, for $P_4O_{10} = 284$.

Experiments numbered 3, 4, 5 and 6 were made at a temperature much higher than 1 and 2. The trustworthiness of 2 is much less than that of the others on account of the small quantity of substance operated on. For the sake of comparison, a determination of the vapour density of mercury was made immediately before the last experiment, and as it gave the value 99·3, it is obvious that the operation was rightly conducted. The numbers for phosphoric anhydride therefore undoubtedly point to the formula P_4O_{10} for this substance, though even at the temperature of bright redness it seems to be only imperfectly gasified.

It seems remarkable that while the 4 atoms of phosphorus remain associated in this compound and in the oxysulphide, $P_4O_6S_4$, discovered by Thorpe and Tutton, the molecule should divide when the whole of the oxygen is replaced by sulphur giving the pentasulphide, P_2S_5 . It is noticeable also that the lower sulphide is represented as P_4S_6 on the evidence of the vapour density (Isambert, *Compt. rend.*, 1886, **102**, 1386). Now, supposing the molecular constitution of the higher sulphide to be P_4S_{10} , and that on vaporisation it dissociates into P_4S_6 and S_4 , the vapour density would have the value (7·67) found by V. and C. Meyer. The boiling point of the so-called pentasulphide is 530°, and Meyer determined the density at a temperature described as a *dark red* ("Die Temperatur war so gewählt, dass das Blei dunkle Rothgluth zeigte," *Ber.*, 1879, **12**, 611). A very low red heat, as shown by fireclay bricks, corresponds to about 700°. The density of sulphur vapour at 606° was found by Biltz, using Dumas' process, to be 4·734; and from estimations through a range of lower temperatures it was found steadily to diminish from 7·937 at 467·9°. It may fairly be supposed, therefore, that the density of sulphur vapour at, say, 650°, assuming this as approximately the temperature of the lead bath in Meyer's experiments on phosphorus pentasulphide, would be somewhat less than 4·7, though not very much less, as it is evident, on plotting Biltz's figures on squared paper, that the curve is very irregular, and that there has been a sudden fall in value from

the figure given immediately before.* Assume the density at a "dark red" heat to have been 4.5, then equal volumes of such vapour and the vapour of P_4S_6 would give a mixture having the mean density of $4.5 + 10.9/2 = 7.7$, which is almost exactly the value found by V. and C. Meyer. The vapour of phosphorus sulphide is brownish-yellow, and, though paler, is similar in colour to sulphur vapour. Altogether the proof that the highest sulphide of phosphorus is a pentasulphide is far from complete, and certainly the density of its vapour cannot be accepted as evidence bearing on the case of the corresponding oxide.

Metaphosphoric acid.

In the course of preparing successive batches of phosphoric anhydride, our attention was repeatedly drawn to the presence of drops of liquid in the front part of the tube when the distillation was conducted at too high a temperature. On these occasions the fused, glassy residue usually left in the platinum boat was not to be seen, and we came to the conclusion that the drops consisted of metaphosphoric acid, and that this compound is far more readily volatile than is commonly supposed. H. Rose, it is true, states (*Annalen*, 1850, **76**, 2, 13, and 1851, **77**, 319) that metaphosphoric acid volatilises at a bright red heat, but it has never been regarded as a compound that could be easily distilled. With the knowledge of this fact, however, we thought that it might be possible to take the vapour density, and that the results would be interesting.

The acid was prepared by dissolving commercial phosphoric anhydride in nitric acid, evaporating the solution in a platinum dish until the liquid ceased to evolve bubbles of vapour, and then boiling away about half of it in a platinum crucible heated to redness. Samples of the residue were then quickly taken out by means of a little platinum dipper, dropped into a small tube of platinum foil, and immediately enclosed in a glass tube, which was sealed up and weighed.

Two determinations of density made at a bright red heat gave the following results.

I.	II.	Calculated for.		
		HPO_3 .	$H_2P_2O_6$.	$H_4P_4O_{12}$.
76.8	78.2	40	80	160

* The three last values given in Biltz's table (*Ber.*, 1888, **21**, 2017) are as follows:—

Temperature.....	580.9°	Density.....	5.607
„	580.9	„	5.412
„	606.0	„	4.734

from which it is clear that great accuracy cannot be claimed for these results.

Experiments showed, however, that the acid prepared in this manner was liable to vary in composition as to the percentage of anhydride it contained. It was therefore necessary to analyse every specimen of the phosphoric acid of which the vapour density was taken; in all cases it was found that it contained a quantity of anhydride in excess of the amount, 88.75 per cent., which corresponds to the formula $(\text{HPO}_3)_n$.

The two following series of experiments were made on two different preparations.

Sample I.

0.0978	gram gave v. d.	71.6	} Mean v. d. = 70.3.
0.1070	,, ,,	69.1	
1.4792	,, 90.18 per cent. of phosphoric anhydride.		

Sample II.

0.0861	gram gave v. d.	69.9	} Mean v. d. = 69.8.
0.0719	" "	69.7	
1.2997	" 90.94 per cent. anhydride	}	Mean = 90.86 per cent. anhydride.
0.7880	" 90.79 " "		

Sample I contains therefore 87.25 per cent. $(\text{HPO}_3)_n$, and 12.75 per cent. anhydride, corresponding to $12\text{H}_2\text{P}_2\text{O}_6, \text{P}_4\text{O}_{10}$; and Sample II has 81.2 per cent. $(\text{HPO}_3)_n$, and 18.8 per cent. of anhydride, corresponding to $8\text{H}_2\text{P}_2\text{O}_6, \text{P}_4\text{O}_{10}$ approximately.

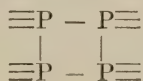
It is obvious from the three series of experiments, that although the composition of metaphosphoric acid varies a little, the vapour of this substance consists chiefly of a dimetaphosphoric acid, $\text{H}_2\text{P}_2\text{O}_6$, which is apparently liable to undergo partial dissociation at a high temperature, and even during ebullition to part with a small quantity of water.

Constitution.

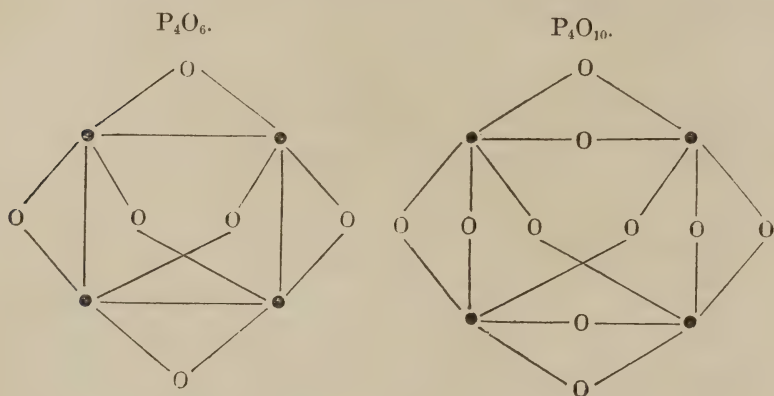
It is, perhaps, idle to speculate as to the possible constitution of compounds such as the oxides and acids of phosphorus, but a few words may not be out of place.

The group of 4 atoms of phosphorus is a very stable form of structure, inasmuch as it bears very high furnace temperatures without breaking up. It is only at a white heat that there is evidence of even incipient dissociation (Biltz and V. Meyer, *Ber.*, 1889, **22**, 725).

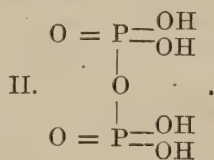
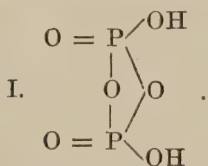
The molecule of phosphorus being represented as



it is evident that there are but 12 units of disposable valency. This can only provide for the accession of 6 atoms of oxygen, unless we assume either the linkage of oxygen to oxygen in a chain, or the disruption of the bond between the phosphorus. The former is so improbable a hypothesis in the present instance that we are reduced to the latter, and the formulæ of the two oxides assume the following shape, in which the dot represents phosphorus.



Formulæ somewhat in this sense have already been suggested for P_4O_6 by Thorpe and Tutton (*Trans.*, 1890, **57**, 563). On the introduction of water the molecule of phosphoric anhydride is divided into two parts, and metaphosphoric acid results, which, from the formula given above for the anhydride, would have the constitution I.



From this the usual formula for pyrophosphoric acid, II, is immediately derived.

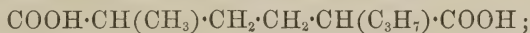
Royal College of Science,
London.

XVIII.—On γ -Phenoxy-derivatives of Malonic acid and Acetic acid, and various Compounds used in the Synthesis of these Acids.

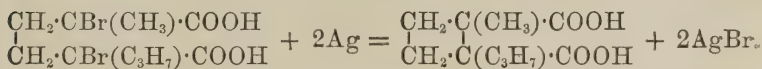
By WILLIAM HENRY BENTLEY, EDWARD HAWORTH, and WILLIAM HENRY PERKIN, jun.

THIS paper contains a description of a number of compounds which were prepared in the course of a research, not yet completed, on the synthesis of methylisopropyltetramethylenedicarboxylic acid, $\text{CH}_2\cdot\text{C}(\text{CH}_3)\cdot\text{COOH}$
 $\text{CH}_2\cdot\text{C}(\text{C}_3\text{H}_7)\cdot\text{COOH}$. This acid possesses especial interest from the fact that its formula was for a long time considered as the most probable expression of the constitution of camphoric acid.

Our idea in attempting to synthesise this acid was to prepare in the first instance α_1 -methylisopropyladipic acid,

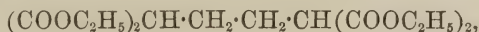


to brominate this acid and then to treat the dibromo-acid thus formed with finely divided silver.

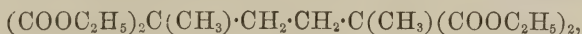


In attempting to synthesise α_1 -methylisopropyladipic acid we have met with unexpected difficulties.

It was known from the work of Bevan Lean (*Trans.*, 1894, **65**, 997; compare also Perkin and Prentice, *Trans.*, 1891, **59**, 819, and Guthzeit and Dressel, *Annalen*, 1890, **256**, 180—188), that, starting with ethylic butanetetracarboxylate,



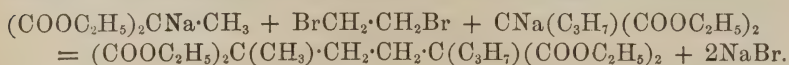
and treating this ethereal salt with sodium ethoxide and methylic iodide, and then again with sodium ethoxide and isopropylic iodide, it was not possible to obtain ethylic methylisopropylbutane tetracarboxylate from which the desired acid could easily have been prepared, because when this ethereal salt (1 mol.) is treated with sodium (1 atom) and methylic iodide (1 mol.) the dimethyl derivative,



is at once produced with regeneration of half of the ethylic butanetetracarboxylate, so that it was found necessary, in order to prepare methylisopropyladipic acid, to resort to indirect methods. The following experiments were therefore instituted, and although many of them gave interesting results, we have not been able, so far, in any

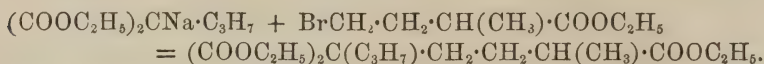
case to obtain sufficient of the methylisopropyladipic acid for analysis and an examination of its properties.

(1) The action of sodium ethoxide and ethylene dibromide (or chlorobromide) on various mixtures of ethylic methylmalonate and ethylic isopropylmalonate was studied in the hope that, in this way, ethylic methylisopropylbutanetetracarboxylate might be formed.



but, at the most, only very small quantities of this ethereal salt could be obtained, and from it no well defined acid could be isolated.

(2) Methylbutyrolactone, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}_3 \\ | \quad \quad | \\ \text{O} \quad \quad \text{CO} \end{array}$, was prepared and converted into *ethylic γ -bromethylmethylacetate* by treatment with hydrogen bromide and subsequent etherification; this ethereal salt was then digested with the sodium derivative of ethylic isopropylmalonate, when it was anticipated that the following decomposition would take place.



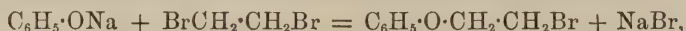
From this ethylic methylisopropylbutanetricarboxylate, the desired acid could then be obtained by hydrolysis and elimination of 1 mol. of carbon dioxide.

Unfortunately, during this reaction, the brom-ethereal salt is evidently for the most part decomposed into methylbutyrolactone and ethylic bromide, so that in this instance again very small quantities only of an ethereal salt of high boiling point were obtained.

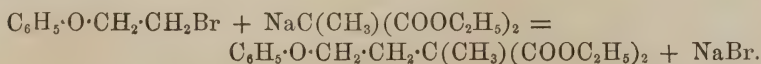
Some considerable difficulty was experienced in preparing methylbutyrolactone, and a number of experiments on the action of glycol chlorhydrin on the sodium compounds of ethylic methylmalonate, and ethylic methylacetoacetate, under widely different conditions, failed to give condensation products from which this lactone might readily have been prepared by hydrolysis.

Ultimately considerable quantities of methylbutyrolactone were obtained in the following way:—

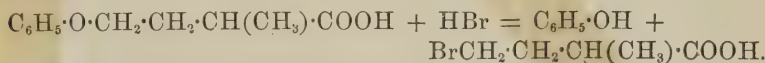
β -Bromethyl phenyl ether was first prepared by the action of ethylene dibromide on sodium phenoxide in alcoholic solution,



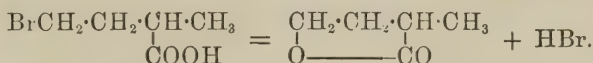
and from this, by digesting it with the sodium compound of ethylic methylmalonate, *ethylic γ -phenoxyethyl- α -methylmalonate* was obtained.



This ethereal salt on hydrolysis yields the corresponding acid, which, when heated at 180°, loses 1 mol. of carbon dioxide with formation of *γ*-phenoxyethylmethylacetic acid, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot COOH$; the latter, by the action of fuming hydrobromic acid, is decomposed into phenol and *γ*-bromomethylmethylacetic acid.

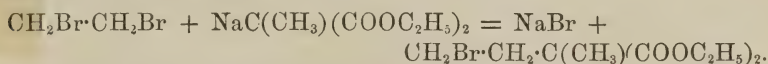


Boiling with sodium carbonate solution readily decomposes this bromo-acid with formation of methyl butyrolactone,

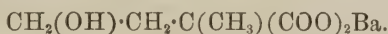


After these experiments had been completed, a paper by R. Marburg appeared in the *Berichte* (1895, 28, 8) describing a different method for preparing methylbutyrolactone, which is briefly as follows:—

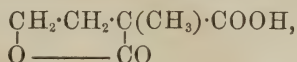
Ethylene dibromide is digested with the sodium derivative of ethylic methylmalonate, when the product of the action is found to contain ethylic *γ*-bromomethylmethylmalonate,



This ethylic salt, on hydrolysis with baryta water, yields the barium salt of *γ*-hydroxyethylmethylmalonic acid,



The free hydroxy acid is not capable of existence, as, on acidifying its barium salt, it at once decomposes with elimination of water and formation of *α*-methylbutyrolactonecarboxylic acid,



and this on dry distillation yields methylbutyrolactone with evolution of carbon dioxide. The properties of the substance prepared in this way are identical with those of the methylbutyrolactone obtained by us by the method described above.

During the course of this investigation many difficulties were encountered which necessitated the preparation and examination of a number of substances which at first sight may appear to have little connection with the synthesis mentioned above. Such of these substances as are mentioned in this communication may be tabulated for the sake of reference, they are the following:—

Glycol phenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$.

β-chloroethyl phenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Cl$.

β-bromomethyl phenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2Br$.

Ethylene diphenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_6H_5$.

Methylene diphenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot O \cdot C_6H_5$.

γ-Phenoxyethylmalonic acid, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH(COOH)_2$.

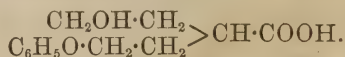
γ-Phenoxybutyric acid, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$.

Butyrolactone, $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH_2 \\ | \quad \quad | \\ O \text{ ————— } CO \end{array}$.

Diphenoxyethylmalonic acid, $(C_6H_5O \cdot CH_2 \cdot CH_2)_2C(COOH)_2$.

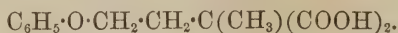
Diphenoxyethylacetic acid, $(C_6H_5O \cdot CH_2 \cdot CH_2)_2CH \cdot COOH$.

β-Phenoxyethyl-*γ*-hydroxybutyric acid,

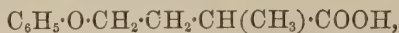


β-Ethoxyethyl phenyl ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot O \cdot C_2H_5$.

γ-Phenoxyethyl-*α*-methylmalonic acid,



γ-Phenoxyethyl-*α*-methylacetic acid,



Methylbutyrolactone, $\begin{array}{c} CH_2 \cdot CH_2 \cdot CH \cdot CH_3 \\ | \quad \quad | \\ O \text{ ————— } CO \end{array}$.

α-Methyl-*γ*-bromobutyric acid, $CH_2Br \cdot CH_2 \cdot CH(CH_3) \cdot COOH$.

A few of the above compounds have been prepared previously, and in these cases we have only given details where we have been able to effect improvements in the preparation.

We are still engaged in experiments on the preparation of methylisopropyltetramethylenedicarboxylic acid, and hope soon to be able to lay before the Society an account of the results obtained.

At the same time we are continuing the examination of some of the substances tabulated above, and especially interesting results are anticipated from the study of the hydrolysis of diphenoxyethylacetic acid.

Glycol Monophenyl Ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OH$.

To obtain this substance, sodium (1 atom) was dissolved in ethylic alcohol, phenol (1 mol.) and glycol chlorhydrin (1 mol.) added, and the mixture heated in a reflux apparatus until neutral. The alcohol was then distilled off, water added, and the product extracted with ether. After washing well, first several times with dilute caustic soda to remove phenol, and afterwards with water, the ethereal solution was evaporated, and the residue distilled under diminished pressure; the whole distilled between 163° and 166° (80 mm. pressure), the yield being very good. A portion boiling at 165° was collected for analysis, and gave the following numbers.

0.1316 gave 0.0864 H_2O and 0.3358 CO_2 . $\text{C} = 69.59$; $\text{H} = 7.28$.
 $\text{C}_8\text{H}_{10}\text{O}_2$ requires $\text{C} = 69.56$; $\text{H} = 7.24$ per cent.

This ether is a colourless, thick, oily liquid, insoluble in water, but readily soluble in ether or alcohol.

β -Chlorethyl Phenyl Ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$.

This has already been obtained by Henry (*Bull. Soc. Chim.*, 1885, 40, 323) by treating potassium phenoxide with ethylene chlorobromide; in preparing large quantities of this compound we operated as follows.

To an alcoholic solution of sodium phenoxide (1 mol.) ethylene chlorobromide (1 mol.) was added, and the mixture heated on the water bath in a reflux apparatus; sodium bromide immediately began to separate, and after about two hours boiling the mixture was neutral. The alcohol was now distilled off, water added, and the product extracted with ether; the ethereal solution, washed with caustic soda to remove phenol, and afterwards with water, was dried over calcium chloride, evaporated, and the residue distilled. The chief portion boiled between 210 and 230° , but there was a considerable residue, which solidified after a time, and consisted of ethylene diphenyl ether (see p. 166); on redistilling the fraction 210 — 230° , it was found that it boiled at 220° , and on standing some time nearly the whole of the distillate solidified to a beautiful white, crystalline mass, melting at 28° .

0.2501 gave 0.2305 AgCl . $\text{Cl} = 22.8$.

$\text{C}_8\text{H}_9\text{OCl}$ requires $\text{Cl} = 22.75$ per cent.

The crystals are very readily soluble in light petroleum, benzene, and alcohol. Henry (*loc. cit.*) gives the melting and boiling points of this substance at 25° and 221° (754 mm.) respectively.

β -Bromethyl Phenyl Ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$.

This substance is prepared in a manner exactly similar to the chlorinated derivative, using ethylene dibromide in place of ethylene chlorobromide. During the operation, large quantities of vinylic bromide, formed from the ethylene dibromide by the removal of hydrogen bromide by the sodium phenoxide, issue from the condenser, and, owing to this secondary action, large quantities of unchanged phenol are found in the product; as this interferes considerably with the fractionation of the product if it is not entirely removed, care must be taken to wash the ethereal solution repeatedly with dilute soda, until it is quite free from phenol. The product is then fractionated under diminished pressure, as the bromide decomposes if distilled under the ordinary pressure. The fraction distilling at

γ -150° (at 40 mm.) is the residue which solidifies is described later. On redistillation, the bromide boiled almost constantly at 144° (at 40 mm.), and gave the following numbers on analysis.

0.2124 gave 0.1991 AgBr. Br = 39.89.

C_6H_5OBr requires Br = 39.8 per cent.

β -Bromomethyl phenyl ether is a white, crystalline substance, melting at 35°. It possesses in a very high degree the property of superfusion, a pure sample having been kept liquid in a bottle for several weeks; on removing the stopper the whole solidified with considerable evolution of heat. The yield of bromide obtained by the above method is about 20 per cent. of the theoretical.

β -Bromomethyl phenyl ether was first prepared by Weddige (*J. pr. Chem.*, 1881, [2], 24, 242), by the action of ethylene bromide on sodium phenoxide, but the details of the preparation and purification as given by him are troublesome; after many experiments the above method of procedure was found to be the most convenient. According to Weddige, the ether melts at 39°, and distils at 240–250°, undergoing decomposition and evolving hydrogen bromide.

Ethylene Diphenyl Ether, $C_6H_5 \cdot O \cdot CH_2 \cdot CH_2 \cdot OC_6H_5$.

The residue left after distillation of the β -brom- (or β -chlor-) ethyl phenyl ether solidifies to an almost colourless crystalline mass, which can be readily crystallised from light petroleum (b. p. 100–120°), in which it is easily soluble on boiling, but almost insoluble in the cold. After repeated recrystallisation, the product melted at 96°, and gave the following numbers on analysis.

0.1402 gave 0.4025 CO_2 and 0.0828 H_2O . C = 78.29; H = 6.56.

$C_{14}H_{14}O_2$ requires C = 78.5; H = 6.54 per cent.

Burr (*Zeit. für Chem.*, 1869, 165), who first prepared this substance, gives the melting point as 98.5°, whereas Lipmann (*Zeit. für Chem.*, 1869, 447) states that it melts at 95°.

Action of Methylene Chloride and Methylene Iodide on Sodium Phenoxide.

Methylene Diphenyl Ether, $C_6H_5 \cdot O \cdot CH_2 \cdot O \cdot C_6H_5$.

These experiments were instituted in the hope of obtaining chloromethyl phenyl ether and iodomethyl phenyl ether, substances which were required for a series of synthetical experiments.

Methylene iodide, CH_2I_2 , and methylene chloride, CH_2Cl_2 , were treated with sodium phenoxide, in proportions theoretically required to form $C_6H_5 \cdot O \cdot CH_2I$ and $C_6H_5 \cdot O \cdot CH_2Cl$. In the former case, the

mixture was heated on the water bath in a reflux apparatus, but when the chloride was used the mixture was heated in soda-water bottles in boiling water for five hours; the product was isolated exactly as described in the case of the preparation of β-bromethyl phenyl ether from ethylene dibromide. In the present case, however, the sodium phenoxide, curiously enough, acts on one half of the iodide or chloride only, and leaves the other half unchanged; methylene diphenyl ether being the sole product of the action. This compound is a colourless, syrupy liquid boiling at 205°, under a pressure of 50 mm. When cooled to 0° it solidifies to a colourless, crystalline mass, which melts at about 15°. The following numbers were obtained on analysis.

0.1187 gave 0.3377 CO₂ and 0.0715 H₂O. C = 77.59; H = 6.69.

0.1523 „ 0.4334 „ „ 0.0810 „ C = 77.61; H = 5.91.

C₁₃H₁₂O₂ requires C = 78.00; H = 6.00 per cent.

Attempts were subsequently made to obtain C₆H₅·O·CH₂Br from the compound just described by treating it with hydrogen bromide under various conditions, but in this we were unsuccessful, as, even when we used the theoretical quantity of hydrogen bromide dissolved in acetic acid, one-half was converted into methylene dibromide and the other half remained unchanged.

Methylene diphenyl ether has been described by Henry (*Ann. Chim. Phys.*, 1883, [5], 30, 269) and by Arnhold (*Annalen*, 1887, 240, 201) as a liquid boiling at 293—295°.

γ-Phenoxyethylmalonic acid, C₆H₅·O·CH₂·CH₂·CH(COOH)₂.

This substance is easily prepared as follows:—Ethyl malonate (13 grams) is added to sodium (2 grams) dissolved in alcohol (25 grams), and the mixture treated with β-bromethyl phenyl ether (14 grams). The whole is then heated on the water bath in a reflux apparatus till neutral, after which it is cooled, diluted with water, and the oil which separates extracted with ether; the ether is evaporated, and the light yellow, oily residue hydrolysed by boiling with alcoholic potash (14 grams) for two hours. The alkaline solution is evaporated with water until all the alcohol has been expelled, and is then acidified and extracted with ether; the ethereal solution is dried over calcium chloride, the ether boiled off, and the resulting oil poured into a basin when it quickly solidifies. Finally the substance is purified by crystallisation from xylene from which it separates in minute needles melting at about 142° with slight evolution of gas.

Analyses.

0.1168 gave 0.2520 CO₂ and 0.0586 H₂O. C = 58.84; H = 5.39.

C₆H₅·O·CH₂·CH₂·CH(COOH)₂ requires C = 58.93; H = 5.35.

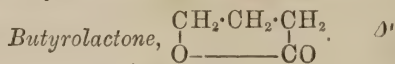
γ -Phenoxyethylmalonic acid is sparingly soluble in cold, readily in hot water; it is very sparingly soluble in benzene, and almost insoluble in light petroleum, but it dissolves very easily in alcohol and ethylic acetate, and is fairly soluble in ether.

γ -Phenoxybutyric acid (γ -Phenoxyethylacetic acid),
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$.

This acid was readily obtained on heating γ -phenoxyethylmalonic acid at 150 – 160° until the rapid evolution of carbon dioxide had slackened, and then finally raising the temperature to 200° for a few minutes; the residual syrup, which was of a pale brownish colour, solidified to a hard mass on cooling. It was easily purified by recrystallisation from light petroleum (b. p. 100 – 120°), from which it separates in thin plates melting at 64 – 65° .

0.1346 gave 0.3282 CO_2 and 0.0808 H_2O . $\text{C} = 66.50$; $\text{H} = 6.67$.
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ requires $\text{C} = 66.66$; $\text{H} = 6.66$ per cent.

γ -Phenoxybutyric acid is sparingly soluble in cold water, easily in hot, and, on cooling, separates in the flocculent condition. It is easily soluble in benzene, ethylic acetate, alcohol, and acetic acid.



A number of experiments were conducted with the object of discovering the best possible means of replacing the phenoxy-group in γ -phenoxybutyric acid by the hydroxy-group; in this case the γ -hydroxybutyric acid formed would immediately lose water, yielding butyrolactone.

The following method gave the best results. γ -Phenoxybutyric acid (25 grams) was gently heated on the water bath with fuming hydrobromic acid (60 c.c.) in a reflux apparatus for about eight hours, and afterwards for the same length of time on the sand bath. On cooling and diluting with water, a heavy black oil separated which was extracted with pure ether, and the ethereal solution washed with water. The ethereal solution was then extracted several times with a strong solution of sodium carbonate, the extracts boiled with animal charcoal for 12 hours, and the liquid filtered from the animal charcoal; the pink filtrate, after being evaporated to a small bulk, was extracted with ether to remove phenol, and then acidified and again extracted repeatedly with pure ether. This ethereal solution was dried over calcium chloride, the ether removed by evaporation, and the residual oil (about 5 grams) fractionated. Practically the whole of the oil distilled between 204° and 206° at the atmospheric pressure, and a sample of the oil boiling at 205° yielded the following results on analysis.

0.1020 gave 0.2090 CO_2 and 0.0646 H_2O . $\text{C} = 55.88$; $\text{H} = 7.03$.

$\text{C}_4\text{H}_6\text{O}_2$ requires $\text{C} = 55.81$; $\text{H} = 6.97$ per cent.

The substance was, therefore, evidently γ -butyrolactone, which, according to Fittig and Roeder (*Annalen*, 1885, **227**, 22), boils at 206° .

Diphenoxyethylmalonic acid, $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOH})_2$.

This acid has been prepared in considerable quantities; the method we usually employed being as follows:—Ethylic malonate (16 grams) is added to sodium (2.3 grams), dissolved in alcohol (30 grams), and the mixture heated with β -bromethyl phenyl ether (20 grams) on the water bath till neutral; the product is then cooled and again treated with sodium (2.3 grams), dissolved in alcohol (30 grams), and β -bromethyl phenyl ether (20 grams), and the mixture once more heated on the water bath till neutral. On adding water, a heavy oil separates; this is extracted with ether, the ether removed by evaporation, and the oily residue hydrolysed by boiling with alcoholic potash (17 grams). After removing the alcohol by evaporation with water, the solution is acidified, and the copious white precipitate of crude diphenoxyethylmalonic acid thus produced is collected, washed with water, and dried on a porous plate until quite free from oily impurity. It is then purified by recrystallisation from 50 per cent. acetic acid from which it separates in rhombic prisms melting and decomposing at 150° .

0.1266 gave 0.3098 CO_2 and 0.0680 H_2O . $\text{C} = 66.44$; $\text{H} = 5.96$.
 $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{C}(\text{COOH})_2$ requires $\text{C} = 66.28$; $\text{H} = 5.81$ per cent.

Diphenoxyethylmalonic acid is almost insoluble in cold water, very slightly soluble in hot water or benzene, and almost insoluble in light petroleum; it is moderately soluble in ether, ethylic acetate, and alcohol, and is extremely soluble in acetic acid. It is reprecipitated by water from its alcoholic and acetic acid solutions.

Diphenoxyethylacetic acid, $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$.

This compound was prepared by heating diphenoxyethylmalonic acid at 180° until carbon dioxide ceased to be evolved; the brown, syrupy residue solidified completely on cooling, and was readily purified by recrystallisation from light petroleum (b. p. 100 – 120°), from which it separated in feathery groups, melting at 88° .

0.1054 gave 0.2788 CO_2 and 0.0625 H_2O . $\text{C} = 72.14$; $\text{H} = 6.59$.
 $(\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CH}\cdot\text{COOH}$ requires $\text{C} = 72.00$; $\text{H} = 6.66$ per cent.

Diphenoxyethylacetic acid is insoluble in cold, and only sparingly soluble in hot, water; it is sparingly soluble in cold, light petroleum,

easily in the hot liquid, and very soluble in benzene, ethylic acetate, alcohol, and acetic acid; its alcoholic and acetic acid solutions yield flocculent precipitates when diluted with water.

β-Phenoxyethyl-γ-hydroxybutyric acid, $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOH}$.

This substance was obtained accidentally in examining the product formed by heating a sample of crude diphenoxyethylacetic acid in a sealed tube with a solution of hydrogen chloride in acetic acid for some hours at about 130° ; the contents of the tube were diluted with water, and the dark, heavy oil which was precipitated was extracted with ether, the ethereal solution washed repeatedly with water to remove acetic acid, and the ether evaporated. The dark, oily residue was then boiled with a strong solution of sodium carbonate for a considerable length of time, in order to remove chlorine. The alkaline solution was now extracted with ether, to remove phenol, acidified, extracted with ether, and the ethereal solution dried with calcium chloride and filtered; shortly afterwards it was observed that crystals were separating from the ethereal solution; these were collected, washed with ether, dried on a porous plate, and recrystallised twice from benzene, in which it dissolves but slightly. It crystallises in prisms, which melt at 112° , but sinter several degrees below this temperature.

0.1083 gave 0.2578 CO_2 and 0.0716 H_2O . $\text{C} = 64.92$; $\text{H} = 7.35$.

$\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{COOH}$ requires $\text{C} = 64.28$; $\text{H} = 7.14$ per cent.

When pure, this substance is almost insoluble in ether, very sparingly soluble in light petroleum, but moderately easily in water.

The *silver salt*, $\text{C}_{12}\text{H}_{15}\text{AgO}_4$, was prepared by precipitating an aqueous solution of the ammonium salt with silver nitrate; it is moderately soluble in hot water, and crystallises on cooling in white tufts.

0.1092 gave 0.0358 Ag. $\text{Ag} = 32.78$.

$\text{C}_{12}\text{H}_{15}\text{AgO}_4$ requires $\text{Ag} = 32.63$ per cent.

With copper sulphate solution, the aqueous solution of the ammonium salt gives a bluish-white precipitate, which dissolves on boiling, and separates out again on cooling, apparently not in the crystalline condition.

Lead acetate solution gives no precipitate at first, but, on standing, a white, crystalline salt gradually separates; this redissolves on boiling, and crystallises out again on cooling.

Barium nitrate and calcium chloride give no precipitate with the aqueous solution of the ammonium salt.

*Action of β -Bromethyl Phenyl Ether on the Sodium Derivative of Ethylic Methylmalonate.**Ethylic γ -Phenoxyethyl- α -Methylmalonate,*
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)(\text{COOC}_2\text{H}_5)_2.$

This substance is obtained when the bromo- or chloro-ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ or $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ (1 mol.), reacts with the sodium derivative of ethylic methylmalonate (1 mol.) in alcoholic solution. In the case of the chloride, the action proceeds slowly, six hours boiling being required to complete it, but in the case of the bromide, it sets in on gently warming, and is so vigorous as to maintain the mixture at the boiling point for some time; when the decomposition is complete, water is added, and the oily product is extracted with ether. The ethereal solution is washed with water, dried over calcium chloride, evaporated, and the residual oil fractionated under reduced pressure, when the bulk of it distils at 230° (45 mm.) as a colourless, thick oil, which, on analysis, gave the following numbers.

0.1392 gave 0.0927 H_2O and 0.3318 CO_2 . $\text{C} = 65.01$; $\text{H} = 7.39$.

$\text{C}_{16}\text{H}_{22}\text{O}_5$ requires $\text{C} = 65.3$; $\text{H} = 7.48$ per cent.

Ethylic γ -phenoxyethyl- α -methylmalonate is a colourless syrup, which, even on long standing, showed no signs of crystallising.

During the fractionation of the crude product of the action of phenoxyethylbromide on ethylic sodiomethylmalonate, a considerable quantity of an oil of low boiling point was obtained, which, on subsequent fractionation under the ordinary pressure, was found to contain, besides ethylic methylmalonate, a liquid free from halogen, and boiling at about 230° . In order to free this substance from ethylic methylmalonate, it was boiled with excess of alcoholic potash for four or five hours, when a large quantity remained unsaponified. Water was added, the oil which was precipitated extracted with ether, the ethereal solution well washed with water, dried, and evaporated. The oily residue thus obtained, when distilled, boiled constantly at 230° under the ordinary pressure. The analytical results agreed with the formula $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OC}_2\text{H}_5$.

0.1502 gave 0.1150 H_2O and 0.3974 CO_2 . $\text{C} = 72.15$; $\text{H} = 8.50$.

$\text{C}_{10}\text{H}_{14}\text{O}_2$ requires $\text{C} = 72.28$; $\text{H} = 8.43$ per cent.

β -Ethoxyethyl phenyl ether is a colourless, mobile oil of penetrating odour, resembling that of benzyl ethyl ether, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OC}_2\text{H}_5$.

 γ -Phenoxyethyl- α -methylmalonic acid,
 $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)(\text{COOH})_2.$

In order to prepare this acid, ethylic γ -phenoxyethyl- α -methylmalonate (50 grams) was boiled with alcoholic potash (50 grams).

There appeared to be very little action in the cold, but, on gently warming, a large quantity of an insoluble potassium salt soon separated; sufficient water was added to dissolve nearly the whole of this, and the mixture boiled on the water bath in a reflux apparatus for two or three hours. Water was then added, the alcohol completely removed by evaporation on the water bath, the residue dissolved in water, cooled, and acidified with hydrochloric acid; the crude γ -phenoxyethyl- α -methylmalonic acid, which then separated as a thick, heavy, brown oil, was extracted with pure ether, and the ethereal solution dried over calcium chloride and evaporated. After standing overnight in a vacuum over sulphuric acid, the oil solidified to a hard crystalline mass, which was readily purified by recrystallisation from hot benzene. The following are the results of the analysis of this substance.

0.1312 gave 0.0684 H_2O and 0.2920 CO_2 . $\text{C} = 60.69$; $\text{H} = 5.79$.

$\text{C}_{12}\text{H}_{14}\text{O}_5$ requires $\text{C} = 60.50$; $\text{H} = 5.88$ per cent.

γ -Phenoxyethyl- α -methylmalonic acid crystallises in colourless prisms which melt at 125° with decomposition and formation of γ -phenoxyethyl- α -methylacetic acid and carbon dioxide. It is sparingly soluble in cold water or cold benzene, and insoluble in light petroleum, but readily soluble in hot water, hot benzene, alcohol, or ether.

γ -Phenoxyethyl- α -methylacetic acid, $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$.

This substance was prepared by heating γ -phenoxyethyl- α -methylmalonic acid at 180° until evolution of carbon dioxide had entirely ceased, and then distilling the residual oil under diminished pressure. The whole distilled between 205° and 210° (45 mm.), the correct boiling point at this pressure being 207° . A small portion of the distillate, which, on cooling, solidified immediately, was recrystallised from light petroleum ($60\text{--}90^\circ$), and thus obtained in the form of small, colourless crystals melting at 80° .

0.1745 gave 0.1100 H_2O and 0.4345 CO_2 . $\text{C} = 67.91$; $\text{H} = 7.00$.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires $\text{C} = 68.04$; $\text{H} = 7.21$ per cent.

This acid is readily soluble in alcohol, ether, or benzene, moderately so in hot water and light petroleum, but only sparingly in the two last-named solvents in the cold.

Silver salt, $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOAg}$.—This was prepared by suspending the acid in water and gradually adding ammonia until the whole had dissolved; the solution was then boiled to get rid of the slight excess of ammonia, and silver nitrate added when the solution was cold. The white, flocculent precipitate thus obtained was collected, washed well with water, spread on a porous plate, and dried in a vacuum over sulphuric acid.

0.0910 gave 0.0382 H_2O and 0.1456 CO_2 . $\text{C} = 43.65$; $\text{H} = 4.66$.
 0.1298 „ 0.0467 Ag. $\text{Ag} = 35.98$.

$\text{C}_{11}\text{H}_{13}\text{O}_3\text{Ag}$ requires $\text{C} = 43.85$; $\text{H} = 4.32$; $\text{Ag} = 35.88$ per cent.

This silver salt is somewhat soluble in boiling water, and separates again, in the amorphous condition, on cooling. A neutral solution of the ammonium salt of γ -phenoxyethyl- α -methylacetic acid gives no precipitate with barium or calcium salts, but, on adding lead acetate, a white, amorphous precipitate is thrown down, which is somewhat soluble in boiling water. With copper sulphate a flocculent green precipitate is obtained insoluble in boiling water.

Action of Bromethyl Phenyl Ether on Ethylic Methylacetoacetate.

This reaction was carried out as follows. Sodium (4 grams) was dissolved in ethylic alcohol (50 grams), the solution cooled, and a mixture of ethylic methylacetoacetate (25 grams) and bromethyl phenyl ether (35 grams) added. In the cold there appeared to be no action, but, on heating on the water bath in a reflux apparatus, sodium bromide quickly separated; the mixture, which, after boiling for about two hours was neutral, was poured into water, and the oily products extracted with ether in the usual way. On distilling the dry product under a pressure of 40 mm. ethylic methylacetoacetate first passed over; the thermometer then rose rapidly, and at 185° almost the whole of the new compound distilled.

0.1400 gave 0.0983 H_2O and 0.3473 CO_2 . $\text{C} = 67.64$; $\text{H} = 7.80$.
 $\text{C}_6\text{H}_5\text{O} \cdot [\text{CH}_2]_2 \cdot \text{C}(\text{CH}_3)(\text{CO} \cdot \text{CH}_3) \cdot \text{COOC}_2\text{H}_5$ requires $\text{C} = 68.10$; $\text{H} = 7.58$ per cent.

Ethylic γ -phenoxyethyl- α -methylacetoacetate is a thick, colourless oil which, on hydrolysis with strong alcoholic potash, yields γ -phenoxyethyl- α -methylacetic acid.

Formation of α -Methylbutyrolactone from γ -Phenoxyethyl- α -methylacetic acid.

γ -Phenoxyethyl- α -methylacetic acid is moderately easily decomposed by heating with mineral acids with formation of α -methylbutyrolactone; the best results being obtained as follows. The pure acid is heated in sealed tubes with a strong solution of hydrogen bromide in glacial acetic acid for six hours at 100° ; the contents of the tubes are then diluted with water, the products extracted with ether, and after the ethereal extract has been washed with water until free from acetic acid, the ether is distilled off, and the residue is boiled with potassium carbonate solution for 12 hours. The phenol formed is then removed by means of ether, the aqueous solution concentrated on the water bath, and, after cooling, acidified and boiled in a reflux

apparatus for two hours, to convert the hydroxy-acid into the lactone. The solution is then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, evaporated, and the product distilled. In this way, a colourless, mobile liquid is obtained which boils constantly at 201° , and is evidently identical with the α -methylbutyrolactone described by Marburg (*Ber.*, 1895, **28**, 10).

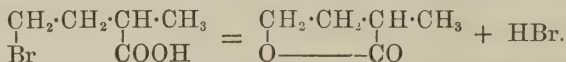
α -Methyl- γ -bromobutyric acid.

In order to prepare this substance, pure α -methylbutyrolactone is left for 24 hours at the ordinary temperature in contact with saturated aqueous hydrobromic acid; the product is poured into water, all rise of temperature being carefully avoided, and the liquid rapidly extracted with ether. After washing well with water, the ethereal solution is dried and evaporated, when a brown, oily residue is left, which cannot be purified by distillation, as it decomposes readily on warming; for analysis it was, therefore, merely left over sulphuric acid in a vacuum for a short time.

0.2732 gave 0.2840 AgBr. Br = 44.04.

$C_5H_9BrO_2$ requires Br = 44.19 per cent.

This acid gives off hydrogen bromide at ordinary temperatures, very probably with formation of α -methylbutyrolactone.



Ethylic γ -Brom- α -methylbutyrate, $CH_2Br \cdot CH_2 \cdot CH(CH_3) \cdot COOC_2H_5$.—The impure γ -brom- α -methylbutyric acid obtained as described above was dissolved in ethylic alcohol and the solution saturated with dry hydrogen chloride; after 24 hours, water was added, the ethereal salt extracted with ether, and the ethereal solution, after being well washed with water and sodium carbonate solution, was dried over calcium chloride, and evaporated. In this case also, the oily residue could not be distilled, for although it did not give off hydrogen bromide so readily in the cold as the acid did, it decomposed rapidly below its boiling point. After standing in a vacuum over sulphuric acid for 12 hours, the bromine was determined.

0.2460 gave 0.2146 AgBr. Br = 37.12.

$C_7H_{13}O_2Br$ requires Br = 38.27 per cent.

Action of Phosphorus Pentachloride on α -Methylbutyrolactone.

In order to study this decomposition, phosphorus pentachloride (20 grams) was gradually added to α -methylbutyrolactone (10 grams), the mixture being well cooled with water during the addition. When all the pentachloride had been added, and the whole

allowed to stand for one hour, the action was completed by heating for one hour on the water bath. On subsequently distilling the product, phosphorus oxychloride passed over first, and then the temperature rose to 189° , at which the rest distilled; there was, however, some decomposition accompanied by charring and evolution of hydrogen chloride. The analysis of the product obtained in this way did not give very good analytical results, although they indicated that the substance was γ -chlor- α -methylbutyryl chloride,



this was borne out by the study of the properties of the chloride.

Anilide of γ -Chlor- α -methylbutyric acid,



This crystalline substance is obtained when the product of the action of phosphorus pentachloride on α -methylbutyrolactone is slowly poured into aniline, the mixture being well cooled during the addition. After standing for one hour, the product is poured into water, dilute hydrochloric acid added until the excess of aniline has been removed, and the whole extracted with ether. The ethereal solution, after being washed successively with dilute hydrochloric acid and with water, is evaporated, and the residue left in a vacuum over sulphuric acid until it gradually deposits crystals. These are freed from oily mother liquor on a porous plate, and then recrystallised from light petroleum (b. p. 100 — 120°). The beautiful white prisms thus obtained melt at 106° .

0.1155 gave 7.0 c.c. moist nitrogen at 18° and 753 mm. $N = 6.96$.

$\text{C}_{11}\text{H}_{14}\text{OClN}$ requires $N = 6.62$ per cent.

*Owens College,
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XIX.—*Note on the Preparation of Glycol.*

By EDWARD HAWORTH, B.Sc., and WILLIAM HENRY PERKIN, Jun.

In preparing glycol by the usual method, namely, digesting ethylene dibromide with potassium carbonate solution, evaporating the product nearly to dryness, and extracting the glycol by means of a mixture of ether and alcohol, a very small yield only is obtained, due principally to the volatility of the glycol with steam, and consequent loss during the evaporation.

As we required a considerable quantity of glycol for some synthetical work, we made many experiments with the object of

improving the method of preparation, and found that by the following simple modifications of the usual process, the yield may be greatly increased.

In the first place, potassium carbonate (138 grams) is dissolved in water (1 litre), and the solution boiled in a stout, round-bottomed flask with ethylene dibromide (188 grams) in a reflux apparatus, from the top of which a glass tube leads to a couple of wash bottles containing bromine. When almost all the oily drops have disappeared (which is usually the case after 8—10 hours), the same quantities of potassium carbonate and ethylene dibromide are again added to the solution, and the boiling continued as before; the operation being repeated until 1128 grams of ethylene dibromide have been decomposed.

After the third addition of ethylene dibromide, crystals of potassium bromide separate on standing over night. These (and those which separate after each succeeding operation) are removed in the morning, by filtration on a vacuum pump, before the action is again started. The crystals are then washed with absolute methylated spirit, the washings being subsequently used for the isolation of the glycol, as explained below. After the decomposition of the ethylene dibromide is complete, the solution of glycol is heated in an oil bath to slowly distil off the water, using a colonna to prevent, as far as possible, loss of glycol by evaporation.

When the distillation has continued some time, the liquid begins to bump violently, owing to the separation of potassium bromide. The solution is now cooled, the crystals of potassium bromide removed, as before, and the distillation then continued. All the water which distils over should be carefully preserved for use in a subsequent preparation. When the solution becomes very viscid, and the temperature of the vapour passing over begins to rise, the distillation is stopped, and the residue is mixed with the methylated spirit employed in washing the potassium bromide crystals, as explained above. After standing for some time, the crystals of potassium bromide, which separate in quantity, are removed by filtration on the pump, washed with absolute methylated spirit, and the combined alcoholic extracts concentrated by slow distillation, as before, from a flask fitted with a colonna.

The residue is then again treated with absolute methylated spirit, which separates more potassium bromide; this treatment is repeated, now using a mixture of alcohol and ether, until almost the whole of the potassium bromide has been removed.

The solvent is then removed by distillation, and the residual glycol fractionated, first under reduced pressure, and finally at the ordinary pressure.

The yield of glycol obtained in this way is about 50—60 per cent. of the theoretical, and we have found it practicable in one apparatus to prepare 1 kilo. of glycol in about 10—14 days.

During the action, considerable quantities of vinylic bromide are formed; this is absorbed by the bromine in the wash bottles, and by subsequently treating the product with dilute potash, to remove the excess of bromine, and fractionation, tribromethylene, $\text{CH}_2\text{Br}\cdot\text{CHBr}_2$, is readily obtained in a pure state.

Owens College,
Manchester.

XX.—*The Oximes of Benzaldehyde and their Derivatives.**

By CHARLES M. LUXMOORE, D.Sc.

It is well known that stereochemical explanations of the isomerism amongst compounds where the carbon is doubly linked to nitrogen, have received less unequivocal support from the behaviour of the aldoximes than from that of other oximido-derivatives. Of the latter, the benzenoid ketoximes may be mentioned as exhibiting in their general deportment a very fair accordance with what stereochemical hypotheses would lead us to expect.

On the other hand, the fact that the isomeric oximes of the benzenoid aldehydes, on methylation, &c., in the usual manner, yield structurally isomeric derivatives as the principal products, offers a difficulty in the way of regarding them as stereoisomers merely. The remarkable results obtained by Dunstan and Dymond (*Trans.*, 1894, 65, 206) by treating paraffinoid aldoximes with phosphorus pentachloride, may be named as another illustration of the abnormal behaviour of oximido-derivatives containing aldehydic hydrogen.

At Professor Dunstan's suggestion I have carried out a series of experiments on the oximes of benzaldehyde, with a view of throwing further light on the nature of their isomerism, and I now communicate the principal results that have been obtained.

Benz-antialdoxime.

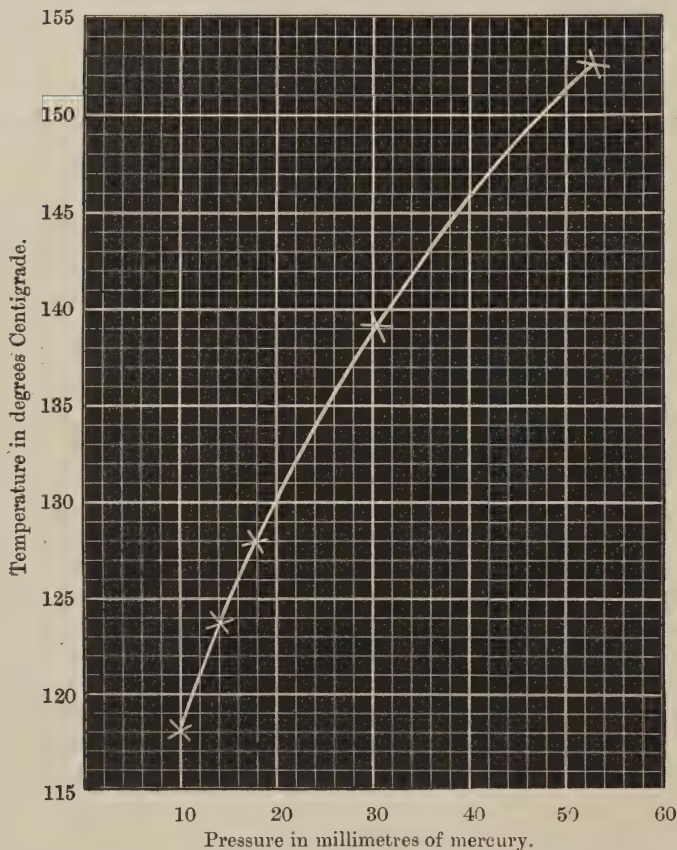
This is most conveniently prepared in the manner described by Beckmann (*Ber.*, 1890, 23, 1684). After being distilled under reduced pressure, the strongly refractive liquid quickly solidifies on

* Part of a thesis accepted for the degree of Doctor of Science of the University of London.

touching it with a crystalline fragment. The melting point of the pure substance recrystallised from light petroleum is 34° ; this is readily depressed several degrees by minute traces of impurities (Dunstan and Luxmoore, *Proc.*, 1894, 253).

The boiling point of benz-antialdoxime is as follows (thermometer in vapour)—10 mm., $118-119^{\circ}$; 14 mm., $123-124^{\circ}$; 19 mm., $128-129^{\circ}$; 31 mm., $138-139^{\circ}$; 53 mm., $152-153^{\circ}$; these results are plotted out on the annexed curve.

Boiling points of Benz-antialdoxime under reduced pressure.



Whether benzaldoxime is formed in the presence of an excess of sodium hydroxide, according to Beckmann's method, or by shaking an aqueous solution of hydroxylamine (made by mixing concentrated solutions of hydroxylamine hydrochloride and sodium carbonate in equivalent proportions) with an ethereal solution of benzaldehyde,

only the anti-modification appears to be formed; no benz-synaldoxime has been obtained in any case.

Benz-antialdoxime Hydrochloride.—This is instantly thrown down as a white pulverulent precipitate when dry hydrogen chloride is passed into an ethereal solution of benz-antialdoxime cooled to 0° . It melts gradually between 103° and 105° . When treated with dilute aqueous ammonia in the presence of broken ice, the oxime collects in oily drops, which are extracted with ether, and the ether allowed to evaporate; on touching the residue with a crystal of benz-antialdoxime it solidifies. The crystals obtained in this manner from the hydrochloride, prepared at zero or below, invariably consisted of benz-antialdoxime, mixed with, at the most, only a minute trace of benz-synaldoxime.

Benz-synaldoxime Hydrochloride.—If hydrogen chloride is passed into an ethereal solution of benz-antialdoxime at the ordinary temperature heat is evolved, and the well-known pearly leaflets of benz-synaldoxime hydrochloride are gradually precipitated. In one experiment, a thermometer, immersed in the solution, rose from 10° to 28° . The same salt is obtained by the action of hydrogen chloride on benz-synaldoxime; purified by recrystallisation from chloroform and light petroleum it melts at 66 – 67° , if heated quickly.

The difference between the isomeric hydrochlorides is at once apparent on moistening them with water (or better with aqueous ammonia); both are dissociated, but whilst the one at once gives rise to oily drops of benz-antialdoxime, the other undergoes no change in appearance, as the liberated benz-synaldoxime is a white crystalline powder. If the acid is not neutralised, this, at the ordinary temperature, is soon converted into oily drops of benz-antialdoxime; in the presence of broken ice, however, even if it is not neutralised, the synaldoxime can be isolated, only slightly contaminated with its isomer, by quickly extracting with ether, washing the ethereal solution, and allowing it to evaporate spontaneously.

Isomeric Transformation of the Hydrochlorides.—On attempting to purify benz-antialdoxime hydrochloride by recrystallisation, it was found that by the mere act of dissolution it was converted into the isomeric syn-hydrochloride. A confirmation of this result was found in the observation that an ethereal filtrate from the preparation of benz-antialdoxime hydrochloride at -10° , when allowed to evaporate spontaneously, deposited a few crystals of the syn-hydrochloride.

Doubtless, therefore, the formation of benz-synaldoxime hydrochloride by the action of hydrogen chloride on benz-antialdoxime is always preceded by the formation of the hydrochloride of the latter, and if kept at or below zero only a trace of this can be dissolved by ether, and the remainder is therefore protected from isomeric change;

at higher temperatures it is more readily dissolved, and thus undergoes rapid transformation into the more stable benz-synaldoxime hydrochloride.

Benz-synaldoxime hydrobromide is obtained when dry hydrogen bromide is passed into an ethereal solution of benz-antialdoxime cooled below 0° . When recrystallised from chloroform and light petroleum, or from acetone and light petroleum, it melts at $77-78^{\circ}$, if rapidly heated. It is a white powder, becoming yellow on exposure to light. 0.157 gram required for neutralisation 7.1 c.c. decinormal ammonia. Calculated for C_7H_6NOH, HBr 7.8 c.c.

Benz-synaldoxime hydriodide is prepared in the same manner, the liquid soon becomes brown from liberated iodine. The hydriodide is unstable, rapidly becoming yellow on exposure to the air. 0.224 gram required 8.6 c.c. decinormal ammonia. Calculated for C_7H_6NOH, HI 9 c.c.

Benz-synaldoxime Dihydrofluoride.—When hydrogen fluoride is passed into an ethereal or chloroformic solution of benz-antialdoxime, this salt is precipitated. Its melting point lies between 50° and 60° , but it is difficult to determine as it decomposes on heating, and melts gradually. 0.193 gram required 22.9 c.c. decinormal ammonia. Calculated for C_7H_6NOH, H_2F_2 23.9 c.c.; for C_7H_6NOH, HF 13.7 c.c.

These three new haloid salts all yielded benz-synaldoxime on regeneration, neither a hydrofluoride, hydromide, nor hydriodide of benz-antialdoxime could be isolated; doubtless these derivatives were first formed, but were instantly transformed into salts of benz-synaldoxime, although the temperature was below 0° .

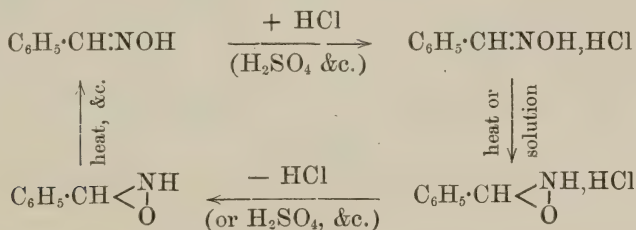
Benzaldoxime Sulphates.—When benz-antialdoxime is gradually added to strong sulphuric acid, the first portions completely dissolve; as soon as a molecular proportion ($C_7H_6NOH = 121$ to $H_2SO_4 = 98$) has been added, the temperature rises, and the whole solidifies to a hard, white, deliquescent mass of benz-synaldoxime sulphate. If, however, sulphuric acid and benz-antialdoxime, both in ethereal solution, are gradually mixed whilst kept in a freezing mixture of ice and salt, an oil separates which is the sulphate of benz-antialdoxime, since it yields the latter by regeneration, when treated with aqueous ammonia at 0° . This oil quickly solidifies, especially on stirring, while the temperature still remains below zero; the solid thus obtained is benz-synaldoxime sulphate.

0.124 gram required 11.7 c.c. decinormal ammonia, and yielded 0.627 gram benz-synaldoxime. Calculated for C_7H_6NOH, H_2SO_4 11.3 c.c. and 0.0681 gram.

The assumption of a structural isomerism between the two oximes of benzaldehyde does not lend itself to an explanation either of the

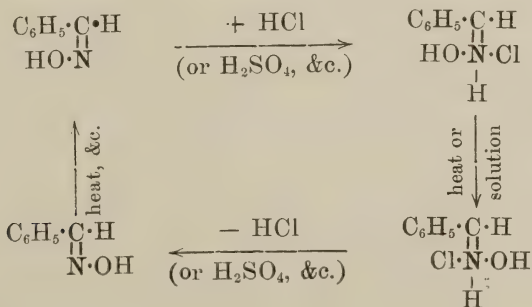
readiness with which the oxime of higher melting point is converted by heat or by dilute aqueous acids into its isomer, or of the reverse change of the hydrochloride, &c., which takes place even more readily, namely, by mere dissolution.

The only structural formulæ available for the oximes of benzaldehyde are $\text{C}_6\text{H}_5\cdot\text{CH}:\text{NOH}$ and $\text{C}_6\text{H}_5\cdot\text{CH} < \begin{smallmatrix} \text{NH} \\ | \\ \text{O} \end{smallmatrix}$. Adopting these formulæ for the oximes melting at 34° and 130° respectively, the changes in question would be expressed by the scheme



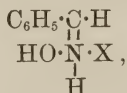
It is difficult to conceive of any reason why the transformation indicated in the left hand column by which the compound, having the isoxime formula, is very readily converted into the normal oxime should be exactly reversed in the hydrochlorides as indicated by the arrow in the right-hand column. If, on the other hand, the isoxime formula be attributed to α -benzaloxime and β -benzaloxime be regarded as the true oxime, a similar scheme, with the arrows reversed, would express the facts, and this would be equally difficult to understand.

On a stereochemical hypothesis, it is not difficult to suggest a partial explanation of the fact that the lability of the aldoximes is reversed in their salts with hydrogen haloïds and sulphuric acid. These salts can be conveniently formulated in the plane of the paper consistently with Pickering's theory (Trans., 1893, **63**, 1069), and the transformation of the oximes clearly expressed as follows.



We may then suppose that, in the oximes themselves, the attraction of hydroxyl to phenyl is greater than to hydrogen, whilst the addition of the elements of hydrogen chloride, for instance, may disturb this equilibrium, because the directive attraction of hydrogen for hydroxyl added to that of phenyl for chlorine is greater than that of hydrogen for chlorine added to that of phenyl for hydrogen.

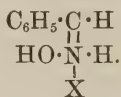
The fact that the hydrobromide and the hydriodide of benz-antialdoxime are less stable than the hydrochloride, suggested that this might be due to the greater mass of the bromine and iodine atoms, and for this reason the action of hydrogen fluoride was tried; but in this case also a syn-derivative only was obtained. As this was a dihydrofluoride, the question cannot be regarded as positively settled. The mass of the radicle X in the anti-alldoxime salt



is approximately as follows:

HX	=	H ₂ F ₂	HCl	HBr	HI	H ₂ SO ₄
X	=	HF ₂	Cl	Br	I	HSO ₄
Mass of X	=	39	35.4	80	127	97

The mass of HF₂ would thus put it after Cl, but very close; while the mass of HSO₄ would put it between Br and I. In neither case is this in accordance with the facts. It is more likely that the greater solubility of the anti-salts that have not been obtained determined their very ready isomeric transformation. The fact, however, that different salts of benz-antialldoxime differ in their degree of stability, suggests that they should be formulated as above, and not with the chlorine, &c., in the median position,



Although Hantzsch (*Ber.*, 1893, **26**, 930) had obtained stereoisomeric hydrochlorides of anisalldoxime and cuminalldoxime, he represents the oximes of benzaldehyde (*Grundriss*, pp. 122, 123) as having

one hydrochloride of the formula $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{C}\cdot\text{H} \\ \parallel \\ \text{H}\cdot\text{N}\cdot\text{Cl} \\ | \\ \text{OH} \end{array}$, with the hydroxyl in the

median position. This perhaps is derived from van't Hoff's conception of pentad nitrogen as situated at the centre of a cube, the valencies being directed to five of its trihedral angles. Van't Hoff does not himself, however, seem to have used this cube for the representation

of oximido-compounds in which pentad nitrogen may be assumed. The fact that there are two hydrochlorides corresponding with parent oximes is best represented by formulæ in which the hydroxyl occupies the same position in the oximes themselves and in their salts, as used above; and, so far as it goes, this is in favour of Pickering's hypothesis rather than of van't Hoff's.

N-Methylbenz-antialdoxime.

When equal quantities of benz-antialdoxime and methylic bromide dissolved in methylic alcohol, are heated at 80–90° for a couple of hours, a hydrobromide of a methyl derivative is obtained which, after recrystallisation from methylic alcohol and ether melts at 67–67·5°

0·4513 gave 0·3856 AgBr. Br = 36·4.

0·2482 „ 14·3 c.c. moist nitrogen at 12° and 766·2 mm. N = 6·87.

$C_7H_6NO \cdot CH_3 \cdot HBr$ requires Br = 37·0; N = 6·48 per cent.

The hydrobromide is readily hydrolysed, even by cold water, the odour of benzaldehyde becoming apparent at once on moistening; it is, therefore, impossible to obtain the base by regeneration in aqueous solution. It was, however, isolated by passing an excess of dry ammonia into an alcoholic solution, precipitating the ammonium bromide by ether, and evaporating to dryness in a vacuum without heat, the residue being redissolved in alcohol and ether added, repeating the process until the ammonium bromide was entirely removed; the methyl derivative was finally separated as a colourless oil by the addition of light petroleum. On stirring, this oil solidified to a waxy mass which could readily be broken up into an apparently amorphous, almost odourless, powder. The substance thus obtained in one experiment melted gradually between 45–49°. This specimen was used for a nitrogen determination.

0·3278 gave 29·4 c.c. moist nitrogen at 13° and 750 mm. N = 10·5.

Methylbenzaldoxime requires N = 10·37 per cent.

The methyl derivative was hydrolysed by distillation with dilute hydrochloric acid; from 2·95 grams, about 1·9 grams of benzaldehyde were obtained, besides a residue of 26 grams of benzoic acid formed by atmospheric oxidation. The hydrochloride obtained weighed 1·6 grams. The equation, $C_7H_6NO \cdot CH_3 + H_2O + HCl \rightarrow C_6H_5 \cdot COH + CH_3 \cdot NH_3OCl$, requires methylhydroxylamine hydrochloride 1·8 grams (found 1·6 grams), benzaldehyde 2·3 grams (found 2·1 grams). The methylhydroxylamine hydrochloride was purified by recrystallisation from methylic alcohol and ether, and was thus obtained in the form of silky needles which were very hygroscopic, and had a powerful reducing action on Fehling's solution. The melting point was found to be 80·5–81·0°, which is lower than that recorded for β

methylhydroxylamine (82—90°), doubtless through the difficulty of obtaining the crystals quite free from moisture. Since the melting point of the isomeric α -salt is 149°, and it has no reducing effect on Fehling's solution, there can be no doubt as to the identity of the product.

The substance was also reduced with hydriodic acid; the hydrochloride of the base formed was hygroscopic, and had otherwise the properties of methylamine hydrochloride. Converted into the platinum-chloride and ignited, 0.3120 gram gave 0.1320 gram platinum = 42.3 per cent. Calculated for methylamine platinumchloride 41.3 per cent.

The new methyl derivative was found to be without constant melting point. A specimen melting, on one occasion, below 68° did not melt, a few days later, below 73°. This was found to be due to the gradual conversion of the substance into the isomeric derivative of benz-synaldoxime. Specimens, after keeping a few days and recrystallising from benzene and light petroleum, showed the correct melting point (81—82°), and had the other properties characteristic of the latter, some of which was prepared for comparison in the manner described by Goldschmidt (*Ber.*, 1891, **24**, 3808).

The isomeric change of the new methyl derivative into the N-methyl derivative of benz-synaldoxime takes place spontaneously in a short time, and without heating, so that the melting point of any specimen depends on the length of time since it was prepared from its hydrobromide, which is perfectly stable. The lowest melting point observed is that of 45—49°, recorded above; the melting point of the pure anti-derivative may, however, be lower than this.

This readiness of isomeric change confirms the conclusion drawn from the products of hydrolysis, that the new derivative is structurally identical with the "nitrogen methyl ether" of benz-synaldoxime, and has the formula $C_6H_5 \cdot CH < \begin{smallmatrix} N \cdot CH_3 \\ | \\ O \end{smallmatrix}$.

That the two substances are not identical is shown (1) by the difference in melting point, (2) by the tendency of the anti-derivative to superfusion, and (3) especially by the very different behaviour of the two derivatives towards water. As already mentioned, all attempts to regenerate the new methyl derivative from its hydrobromide in the presence of water failed on account of the great readiness with which it is hydrolysed even by cold water. The methyl derivative itself is also hydrolysed by water when freshly prepared, and gives an almost immediate reduction with Fehling's solution in the cold, although it loses this property if kept, in consequence of its conversion into the syn-derivative; the latter, on the contrary, is perfectly stable towards water and neutral saline solutions, being in fact

obtained by the dissociation of its sodium iodide compound by the action of water or of solution of sodium chloride.

It must also be observed that the hydrobromide of the new methyl derivative is formed from the anti-oxime under circumstances in which the syn-oxime cannot exist, whilst the methylimido-derivative of the syn-oxime is obtained in a manner which in no way renders it likely that the latter should be converted into the isomeric benz-antialdoxime.

Methylic iodide, when heated with benz-antialdoxime, also combines with it to form the corresponding hydriodide; this generally resembles the hydrobromide in its properties, but is very difficult to purify in consequence of the readiness with which it becomes coloured by the liberation of iodine. Methylic chloride, on the other hand, does not react with benz-antialdoxime; neither does ethylic iodide, so that it has been impossible to obtain an ethyl derivative in this manner.*

The hydrobromide of the so-called "nitrogen methyl ether" of benzsynaldoxime was prepared for the sake of comparison. It melts at 66—67°, that is to say, at almost the same temperature as the hydrobromide obtained from benz-antialdoxime and methylic bromide.

As it was possible this might be the same substance formed by hydrogen bromide having caused isomeric change in the reverse direction, the regeneration was conducted in the absence of water in the manner previously described; the quantity was small, and the whole of the operations were completed in a very short time, so that if the anti-methyl derivative had been the product of regeneration no time was allowed for its isomeric transformation back into the syn-derivative. The crystals of the base thus obtained, after merely draining for a few moments on a tile, and without being recrystallised, melted at 82—83°. Moreover, after boiling with water and cooling, they did not reduce Fehling's solution, showing that they were not hydrolysable by water. Evidently, therefore, they consisted of the nitrogen methyl derivative of benz-synaldoxime, and the two hydrobromides are distinct substances, though melting at about the same temperatures.

It is well known that in the usual method of methylating benz-antialdoxime by adding sodium methoxide and methylic iodide successively, the action being carried out on a water bath, the methoxy-

* There is no record of any previous experiments being made to bring about the addition of the elements of an alkylic haloid to an oxime by heating them together. An attempt was therefore made to extend this reaction so as to make it available for the preparation of the little known alkyl isoximido-derivatives of the ketoximes, but without success. Benzophenoxime heated with methylic iodide at 90° was not acted on; at a higher temperature, there was so much decomposition that the hydriodide of the methyl derivative could not be isolated. Methylamine, however, was obtained on reducing the product of the action, showing that an isoximido-derivative had been formed.

derivative of benz-antialdoxime, $\text{C}_6\text{H}_5\cdot\text{CH}\cdot\text{NO}\cdot\text{CH}_3$, is almost the only product. As it seemed likely that the preformation of the sodium salt was in a great degree, at any rate, the cause of this, a few experiments were made to see whether the new methyl derivative would be obtained if the conditions of the experiment were slightly altered. To a mixture of methylic iodide with benz-antialdoxime, the calculated quantity of sodium methoxide dissolved in methylic alcohol was gradually added in the cold; the characteristic fruity odour of the oxygen methyl ether was at once apparent. A test portion of the product gave, after boiling with water and cooling, a notable reduction of Fehling's solution, due, doubtless, to the presence of the new nitrogen ether. It was, however, found impossible to isolate this; but the isomeric syn-derivative, into which it passed, was separated in the form of its sodium iodide compound. That this was not the first product of the action is proved firstly by the ease with which specimens of the product, tested shortly after its formation, were found to be hydrolysed by water; and, secondly, because, as was found in a separate experiment, benz-synaldoxime cannot exist in the presence of methylic iodide, so that a derivative of the latter oxime could only be formed from an anti-derivative first formed. Altogether, about 10 per cent. of the methyl derivative formed had the isoximido-structure, in other words, about 1 molecule in 10 was caught in the tautomeric form expressed by the formula



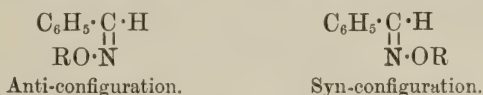
A review of the alkyl derivatives of the oximes furnishes conclusive evidence of the existence of isomerism which structural formulæ are insufficient to represent. The benzenoid aldoximes form two series of alkyl derivatives having the true oximido-structure, $\cdot\text{NOH}$, and yielding identical products of hydrolysis and reduction; the chief distinctions between the corresponding alkyloxy-derivatives of anti- and syn-aldoximes lie in their melting and boiling points.

The chief products, however, of the action of alkylic iodides and sodium alcoholates on syn-aldoximes are the so-called "nitrogen ethers," in which there is evidence of direct linking between alkyl and nitrogen. No evidence of the existence of such isoximido-derivatives of the antialdoximes has hitherto been forthcoming, the supposed isomeric benzylimido-derivative of furfuraldoxime which Werner (*Ber.*, 1890, **23**, 2336) assumed to be an anti-derivative having been shown by Goldschmidt (*Ber.*, 1892, **25**, 2573) to be a compound of the syn-derivative with water of crystallisation. The methyl derivative obtained from benz-antialdoxime by the action of methylic bromide being structurally identical with that obtained from

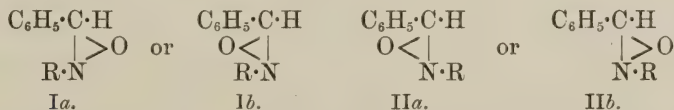
benz-synaldoxime by the action of methylic iodide and sodium methoxide, completes the set of four methyl derivatives obtainable from the oximes of benzaldehyde.

Thus there are four distinct series of derivatives, two of which have the oximido- and two the isoximido-structure, whilst one of each pair is an anti- and the other a syn-derivative. For these four methyl derivatives of the oximes of benzaldehyde, only two structural formulæ are available.

It seems, therefore, necessary to admit some other cause of isomerism amongst the alkyl derivatives of the benzenoid aldioximes than can be expressed by structural formulæ. Without attempting to draw any definite conclusions as to the exact disposition of the atoms in space, we may accept as a working hypothesis the assumption that the isomerism that cannot be satisfactorily accounted for by different modes of atomic linking is due to a condition of asymmetry in the molecule, the hydrogen or alkyl being nearer to the aldehydic hydrogen in the one isomer, and to the phenyl in the other. In true oximido-compounds this will be represented by the following configuration formulæ in the plane of the paper.



The same isomerism would obtain amongst the isoximido-compounds, which we may express by the formulæ

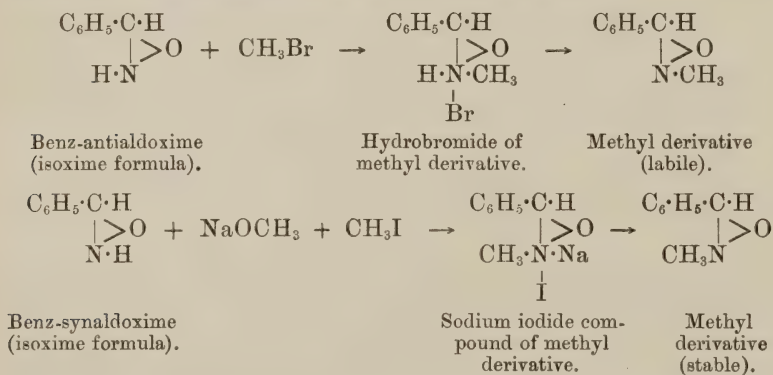


But the formulæ Ia and Ib must be taken to be identical, as must the formulæ IIa and IIb, as it is simplest to assume that the oxygen and its two valencies are in the same plane (at right angles to the plane of the paper) as that containing the nitrogen and carbon atoms and the four valencies by which they are linked to each other and to oxygen.

Whilst it seems clear that stereoisomerism exists amongst the alkyl derivatives of the benzenoid aldioximes, and it is therefore reasonable to admit that it also obtains amongst the oximes themselves, it cannot be denied that this is an incomplete explanation of the isomerism of the two oximes of benzaldehyde, since it fails to account for the fact that the principal products of their methylation in the usual manner have different structures. Hantzsch, indeed, maintains (*Grundriss der Stereochemie*, p. 113) that the :NOH formula represents the normal structure of both oximes, and that the formation of

isoximido-derivatives is due to the action of water; and Goldschmidt (*Ber.*, 1891, **24**, 2808), in his description of the sodium iodide compound formed when benz-synaldoxime, methylic iodide, and sodium methoxide react, gives a very ingenious explanation of the way in which he supposes the isoximido-methyl derivative to be formed from the parent substance supposed to have the normal structure :NOH. But the formula which he gives to the intermediate sodium iodide compound is very improbable, and his explanation cannot be regarded as valid. The fact that, when benz-antialdoxime and methylic bromide are heated together (in the absence of water), the hydrobromide of the isoximido-methyl derivative is formed, completely disproves this statement of Hantzsch's, for it shows that both oximes are very ready to react in the sense of the isoximido-formula, though the benzsynaldoxime does so more readily than its isomer.

It seems likely that Goldschmidt's sodium iodide compound is formed by the addition of the elements of methylic iodide to the sodium derivative of the syn-oxime with the isoxime structure, in a manner analogous to the formation of the hydrobromide of the methyl derivative from benz-antialdoxime. If we represent these changes according to positional formulæ we get the scheme



That is, the anti-alldoxime yields a methyl derivative having the syn-configuration, and the syn-alldoxime yields a derivative having the anti-configuration. Although this appears to be supported by the fact that the anti-derivatives generally (exclusive of those containing pentad nitrogen) are more stable than the corresponding syn-derivatives, nevertheless it is not sufficiently certain to justify any change of name, and it will be wise, therefore, to continue to designate these methyl derivatives after the parent alldoxime.

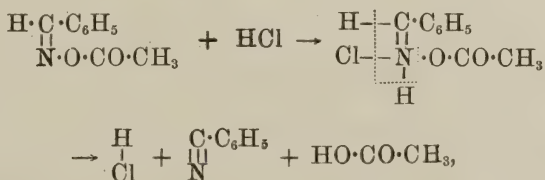
Acetylbenz-antialldoxime.

This substance, prepared by the action of acetyl oxide on crystal-

lised benz-antialdoxime, can be solidified by cooling to -10° and persistently stirring, although it has been described as an oil by previous observers; it melts between 14° and 16° . That this crystalline substance was a true derivative of the anti-oxime was established by regeneration.

When dry hydrogen chloride is passed into a cooled ethereal solution of acetylbenz-antialdoxime, benzonitrile is formed, as stated by Minunni (*Gazzetta*, 1892, **22**, ii, 174); in many cases benzamide is also obtained, and sometimes a hydrochloride of benzamide is precipitated, even when every trace of water is most carefully excluded. A number of experiments have been made to elucidate this action, and it has been ascertained that the latter are secondary products. In view of the difficulty of accounting for the formation of benzamide in the absence of moisture, a direct experiment was made to determine whether the elements of water could be abstracted from acetic acid by benzonitrile in the presence of hydrogen chloride with the concurrent formation of acetyl chloride or acetyl oxide. The acetic acid used was freed from water by mixing it with excess of acetyl oxide, and repeatedly redistilling till it boiled constantly at 119° . It was then mixed with benzonitrile and ether (distilled over sodium) and dry hydrogen chloride passed in, the whole being allowed to remain for a short time, and then fractionally distilled. Benzamide (m. p. 128°) was obtained equivalent to about half the benzonitrile taken. The early fractions of the distillate appeared to indicate that probably both acetyl chloride and acetyl oxide had been formed.

Whilst Minunni's experimental results are thus confirmed, the conclusions he draws from them, in opposition to Hantzsch's use of the acetyl derivative as a criterion of configuration, do not appear to be adequately supported. As the hydrogen chloride is evidently a potent factor in the action, it would seem reasonable to suppose that a compound is at first formed which is of a very unstable nature, and which, by immediate loss of the elements of hydrogen chloride and hydrogen acetate, yields benzonitrile. Assuming the hydrogen chloride to be added on somewhat in the same way as in the salts of the oximes, we get the following scheme.



in which the remaining affinities of pentad nitrogen are made use of according to Pickering's theory.

My attempts to isolate such an intermediate compound have been unsuccessful, and, therefore, it would not be proper to lay too much stress on the above explanation; however, such a compound would, of course, be very unstable, and the above considerations seem sufficient to show that Minunni's objection to the stereochemical representation of the aldoximes cannot be maintained by means of this decomposition.

Action of Phosphorus Pentachloride on Benzaldoximes.

An excess of phosphorus pentachloride was gradually added to an ethereal solution of benz-antialdoxime kept below -8° by a freezing mixture. A small quantity of a white powder was precipitated, probably benz-antialdoxime hydrochloride. The orange-coloured liquid was poured into ice-cold water and the mixture distilled; in the aqueous portion of the distillate, formic acid was identified, an aliquot portion yielding, with mercuric chloride, a precipitate corresponding to 0.03 gram on the whole quantity. An oil had also come over which was a mixture of benzaldehyde and benzonitrile; the latter, when hydrolysed with potassium hydroxide, gave a quantity of ammonium chloride corresponding to 2.1 grams of benzonitrile on the whole quantity. Hydroxylamine and aniline were identified in the residue from the original distillation. Benz-antialdoxime had thus yielded, under the influence of phosphorus pentachloride, the hydrolytic products of formanilide 0.08 gram, and benzonitrile 2.1 grams, and some oxime had been regenerated.

Benz-synaldoxime, treated in the same way, gave similar results. 0.06 gram of formanilide and 2.3 grams of benzonitrile were obtained besides regenerated oxime. The formation of formanilide as a product of the action of phosphorus pentachloride on the oximes of benzaldehyde does not appear to have been noticed by previous workers, but it was, of course, probable considering that the formation of formamide from acetaldoxime had been observed by Dunstan and Dymond (*loc. cit.*). It is, nevertheless, very difficult to explain this result. In the first place it is quite clear that benz-antialdoxime is not in this experiment converted into benz-synaldoxime by the action of hydrogen chloride, for it has been shown that at these low temperatures the anti-hydrochloride suspended in ether is stable; moreover, the quantity of hydrochloride precipitated is only very small. If, however, in the experiment with benz-antialdoxime, it be assumed that either the hydrogen chloride formed, or the phosphorus pentachloride favours the transformation into the synaldoxime, so that the benzonitrile is formed as the result of the action of the pentachloride on the latter, then it would be necessary to make a further assumption that in the experiments with benz-synaldoxime under identical con-

ditions, the same reagent favoured a transformation of part of the synaldoxime into anti-aldoxime which yielded the formanilide.

It seems more reasonable to assume that the action of phosphorus pentachloride in some way removes the cause that makes the stereoisomerism possible. For instance, it may combine in a loose way with the oxime, so that the latter ceases to have a double link between carbon and nitrogen, and the action goes on mainly in the sense of the most favoured (syn) configuration, whilst a small proportion of the molecules are caught in the less favoured configuration, and undergo the Beckmann transposition, yielding formanilide.

Action of Phosphorus Trichloride on Benz-antialdoxime.

On adding phosphorus trichloride to a cooled ethereal solution of benz-antialdoxime a white precipitate of hydrochloride is thrown down, and the filtrate, having been poured into water and neutralised with sodium hydroxide, is found to contain much benzonitrile, but to regenerate a certain quantity of the oxime. By reversing the process, and adding the oxime to a large excess of phosphorus trichloride, less of the hydrochloride is precipitated, but still the elements of hydrogen chloride are eliminated from some of the chlorine compound, so that the product of the action consists of a mixture of the very unstable chlorine substitution compound, $C_6H_5 \cdot CHNCl$, benzonitrile, and the excess of phosphorus trichloride. From this mixture it is impossible to isolate the new compound, as there is no means of separating it from the benzonitrile. Its presence was, however, proved by decomposing the phosphorus trichloride with the least possible quantity of water, and then, after distilling off the ether under diminished pressure and extracting the residue with light petroleum, in which hydrogen phosphite is insoluble, the solution thus obtained was freed from the last trace of phosphite compound by shaking with a drop of water; on now decomposing it by sodium hydroxide, it was found to contain a considerable quantity of chlorine, evidently from the presence of the chlorine substitution compound $C_6H_5 \cdot CH : HO \cdot N$.

This compound was ultimately obtained as follows. Benz-antialdoxime, dissolved in a very little ether, was gradually added to a large excess of phosphorus trichloride below 0° ; the precipitate formed, supposed to be the hydrochloride of the oxime, was filtered off, but after a few minutes it became liquid, and had the characteristic odour of benzonitrile. As it seemed likely that this was the compound which it was desired to isolate, and that had thus evolved its hydrogen chloride on exposure, the experiment was repeated using scarcely any ether at all. The precipitate which was formed was set to drain in a beaker well surrounded by a freezing mixture, but it

presently began to evolve hydrogen chloride with almost explosive violence, and after standing in a desiccator for a short time the residual liquid gave, on hydrolysis, no trace of hydroxylamine, all the oxime having been converted into nitrile. In these experiments, no hydrogen chloride was evolved while the oxime was being added to the phosphorus trichloride, and no hydrochloride of the oxime was formed.

The chlorine substitution compound of benz-antialdoxime,

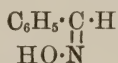


is therefore a white solid, nearly insoluble in phosphorus trichloride, moderately soluble in ether. In the pure state it decomposes into benzonitrile and hydrogen chloride below 0° , but can be kept for a short time in dilute solution.

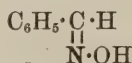
Action of Phosphorus Trichloride on Benz-synaldoxime.

When phosphorus trichloride is added to an ethereal solution of benz-synaldoxime at -10° , half of the oxime is instantly converted into benzonitrile, the other half being converted into the hydrochloride by the hydrogen chloride which is eliminated. If the filtered liquid is poured into water, no oxime is regenerated. Thus the compound formed by the substitution of chlorine for hydroxyl in benz-synaldoxime is so unstable as to be incapable of existence; it instantly decomposes into benzonitrile and hydrogen chloride, and although the latter combines with more oxime, if any is present, to form the hydrochloride, this has no share in effecting the decomposition. This was proved by adding benz-synaldoxime in small portions to a large excess of phosphorus trichloride; hydrogen chloride was freely evolved, and only a comparatively small quantity of hydrochloride was precipitated. This experiment was carried out so as to be strictly comparable with that in which the chlorine substitution compound was obtained from benz-antialdoxime, but no corresponding derivative could be obtained. It evidently breaks up at the moment of its formation.

Evidently this difference of behaviour between the two oximes when treated with phosphorus trichloride, confirms the configuration formulæ assigned to them.



Benz-antialdoxime, m. p. 34° .



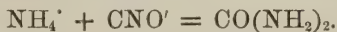
Benz-synaldoxime, m. p. 130° .

This investigation was carried out at the Research Laboratory of the Pharmaceutical Society, and I desire to express my warmest thanks to Professor Dunstan, not only for many valuable suggestions, but also very especially for his kind and unfailing encouragement.

XXI.—*Transformation of the Alkylammonium Cyanates into the corresponding Ureas.*

By JAMES WALKER, D.Sc., Ph.D., and JAMES R. APPLEYARD, F.C.S.,
University College, Dundee.

It has been shown by Walker and Hambly (Trans., 1895, **67**, 746) that the production of urea from an aqueous solution of ammonium cyanate is not a case of simple transformation of one molecule into another, but that the law regulating the transformation is the law of a bimolecular action, the active molecules being in all probability ammonium ions and cyanic acid ions. To use Ostwald's notation, the equation which expresses the action is



The velocity constant of the transformation is given by them for different temperatures, and in the present paper a comparison is effected between that constant and those obtained when the hydrogen atoms of the ammonium ion are replaced by alkyl radicles.

The experiments were all made with decinormal solutions, which were prepared in the manner described by Walker and Hambly. The alkylammonium chloride was agitated for an hour with excess of silver cyanate and the requisite quantity of water, after which the solution was filtered, and portions tested, with nitric acid and silver nitrate on the one hand, and with nitric acid and potassium chloride on the other, in order to prove the absence of soluble silver salt and soluble chloride respectively. By operating in this way, the solutions obtained were not always precisely decinormal, but in such cases the experimental numbers have been reduced to a uniform value by applying the very slight correction necessary, so that all the numbers given in the tables which follow are comparable with each other. Experiments were made at one temperature only, namely, at 59.6°, except when equilibrium points or reverse actions were being determined.

Ethylammonium Cyanate.

A decinormal solution of ethylammonium cyanate was heated at 59.6°, 5 c.c. of it being removed from time to time, and added to 5 c.c. of a decinormal solution of silver nitrate. After the mixture had cooled, the precipitated silver cyanate was filtered off, and the amount of silver in the filtrate determined by means of a N/50 solution of ammonium thiocyanate. In order to ascertain the point at which the action ceased, a decinormal solution of ethylurea was heated at 100°, and the amount of cyanate formed ascertained in the same way as in the direct action. The time which elapsed from the commence-

ment of the heating is given in minutes under t , in the following table, the titres being given in the second column, and the actual concentration of the urea in the third.

t .	Titre.	Urea present.
0	25.0	0.1000
30	24.05	0.0962
80	23.6	0.0944
140	23.05	0.0922
200	22.95	0.0918
260	22.8	0.0912
320	22.9	0.0916

Ethylurea differs from urea in giving no perceptible quantity of carbonate when heated for a considerable time with water at 100° . After 260 minutes, the solution was found to possess a feeble ammoniacal smell, and a slight alkaline reaction, but it gave no precipitate with calcium nitrate. We are thus enabled to fix the end-point with accuracy, the concentrations for equilibrium being 0.0912 normal ethylurea, and 0.0088 normal ethylammonium cyanate.

Walker and Hambly found, for the direct transformation of ammonium cyanate, that the expression $\frac{1}{t} \cdot \frac{x}{E-x}$ remained constant, E being the end-point, and x the titre. This also holds good for ethylammonium cyanate, as may be seen from the following table.

Ethylammonium Cyanate. $E = 22.8$.

t .	x .	$E - x$.	$\frac{1}{t} \cdot \frac{x}{E - x}$.
30	4.95	17.85	0.0093
50	7.35	15.45	0.0096
70	9.1	13.7	0.0095
100	11.2	11.6	0.0097
130	12.6	10.2	0.0095
Mean			0.0095

The value of the expression $\frac{1}{t} \cdot \frac{x}{E-x}$ for ammonium cyanate at 59.7° is 0.0144, the end-point being practically the same, namely, 22.9. It thus appears that the transformation of ethylammonium cyanate into ethylurea proceeds more slowly than the transformation of ammonium cyanate into ordinary urea, as a direct comparison of the titres at corresponding times will also show. The values of the constants in the above instance are nearly proportional to the rates at which the actions start, and this arises from the practical identity of the end-points. In the calculation, the progress of the reverse action

(transformation of urea into cyanate) has been neglected, but this neglect does not invalidate the comparison of the rates of the direct actions when the end-points have nearly the same value. When the end-points are widely apart, however, as they are in the case of other alkyl derivatives, the reverse action must be taken into account, if the comparison is to be of any value; indeed, it is otherwise impossible to obtain a constant when the point of equilibrium is far removed from the urea end. This greatly complicates the calculation, but the expressions obtained give the true velocity constants.

If A is the original concentration of the cyanate expressed in terms of a normal solution, the active mass of the ammonium ions will be A , which is also the active mass of the cyanic ions, supposing the ammonium cyanate to be fully dissociated. This is not quite the case,* but as all the ammonium cyanates considered may be assumed to be equally dissociated in equivalent solutions, the comparison of the numbers obtained is not thereby affected. Let the quantity x have been transformed into urea at the time t ; then the rate at which the direct reaction will proceed is

$$(1). \quad \frac{dx}{dt} = k(A - x)^2.$$

But at the same time we have the reverse reaction proceeding according to the equation

$$(2). \quad -\frac{dx}{dt} = k'x,$$

so that for the real progress of the action we have

$$(3). \quad \frac{dx}{dt} = k(A - x)^2 - k'x.$$

At the equilibrium point, $\frac{dx}{dt} = 0$, therefore

$$(4). \quad \begin{aligned} k(A - \xi)^2 &= k'\xi, \text{ or} \\ K &= \frac{k'}{k} = \frac{(A - \xi)^2}{\xi}, \end{aligned}$$

where ξ is the value of x at the point of equilibrium. K , the ratio of the velocity constants of the opposed reactions, is thus easily determined by means of the end-point experiment.

Substituting kK for k' in (3) we have

$$\frac{dx}{dt} = k\{(A - x)^2 - Kx\},$$

or

$$\frac{dx}{x^2 - (2A + K)x + A^2} = kdt.$$

* At the dilutions investigated, the degree of dissociation averages 90 per cent., with a variation from the mean of 4 per cent.

Integrating the expression on the left hand side by partial fractions, and bearing in mind that for $t = 0$, $x = 0$, we obtain as the value of k ,

$$\frac{1}{2t} \cdot \frac{1}{\sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}} \log_e \frac{A^2 - x \left(A + \frac{K}{2} - \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}{A^2 - x \left(A + \frac{K}{2} + \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}.$$

or, if we use decadic, instead of natural, logarithms,

$$(5). k = \frac{1.15}{t \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}} \log \frac{A^2 - x \left(A + \frac{K}{2} - \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}{A^2 - x \left(A + \frac{K}{2} + \sqrt{\left(A + \frac{K}{2}\right)^2 - A^2}\right)}.$$

The expression, although complicated, is sufficiently convenient for calculation in the form given. The value of k' is obtained from the equation $k' = Kk$.

In the case of ethylammonium cyanate, the value of A is 0.1, and of ξ 0.0912; so that from (4) we have

$$K = \frac{(0.1 - 0.0912)^2}{0.0912} = 0.00085.$$

If we now write the table for the transformation with the values of x in terms of a normal solution, and calculate the values of k by means of equation (5) we obtain it in the following form.

t .	Titre.	x .	k .
30	4.95	0.0198	0.081
50	7.35	0.0294	0.083
70	9.1	0.0364	0.082
100	11.2	0.0448	0.081
130	12.6	0.0504	0.079

Mean..... 0.081

The expression given in equation (5) is thus constant, the mean value of k being 0.081. For k' we have $0.081 \times 0.00085 = 0.000069$. These constants give the amounts transformed in one minute when the original concentration is normal, and is maintained at that value. Thus 8 per cent. of a normal solution of ethylammonium cyanate would be transformed into ethylurea in one minute at 59.6° , if the concentration did not fall off as the action proceeded; whilst of a normal solution of ethylurea only 0.007 per cent. would be re-transformed into cyanate under the same conditions.

The value obtained for $\frac{1}{t} \cdot \frac{x}{E-x}$ in decinormal solution was 0.0095,

and this for a normal solution would become 0.095. It will be seen, therefore, that by neglecting the reverse action, the value of the simple constant is considerably greater than that of the real constant; and this divergence becomes more marked as the rate of the reverse action increases.

With ammonium cyanate itself, it is difficult to ascertain the actual constant k , because not only is there a reverse reaction, but a slow secondary transformation of cyanate into carbonate. Taking the "practical" end-point as the basis of calculation (Walker and Hambly, *loc. cit.*, 751), the values of the constant C is by the reverse action made greater than k , but by the subsidiary transformation it is made less than k . As these two disturbing influences nearly balance each other in amount, the observed value of C , namely $10 \times 0.0144 = 0.144$, must be very nearly equal to k , so that for the transformation of ammonium cyanate we may put $k = 0.144$. The real end-point (*loc. cit.*, 750) lies at 95 per cent., and so for ξ we have 0.095, and for K , $\frac{0.005^2}{0.095} = 0.000263$, giving us $k' = 0.144 \times 0.000263 = 0.000038$. These results show that whilst the transformation of the ethylammonium cyanate is more rapid than that of the ammonium cyanate, the reverse transformation of the ethylurea proceeds more slowly than is the case with urea itself.

Methylammonium Cyanate.

When a decinormal solution of methylurea is heated for half an hour at 100° , it gives on cooling only a faint turbidity with silver nitrate solution. The titre of the filtered solution (see p. 193) after heating for 120 minutes was found to be 23.9, and after 150 minutes, 24.0. The composition of the solution at the equilibrium point is thus 96 per cent. methylurea and 4 per cent. methylammonium cyanate, the value of ξ being, therefore, 0.096. For K , we have $\frac{0.004^2}{0.096} = 0.000166$.

Calculating the value of k from the formula given in equation (5) we obtain the following table from the experimental numbers for the direct transformation.

t .	Titre.	x .	k .
10	3.0	0.0120	0.141
20	5.3	0.0212	0.135
35	7.7	0.0308	0.129
50	9.9	0.0396	0.133
80	12.8	0.0512	0.132
110	14.9	0.0596	0.135
Mean.....			0.134

The value of k' is $0.134 \times 0.000166 = 0.000022$. These numbers show that the direct transformation proceeds more rapidly in the case of methylammonium cyanate than in the case of the ethyl compound, the reverse being the fact for the retransformation of the corresponding ureas.

Diethylammonium[†] Cyanate.

Unsymmetrical diethylurea, $\text{NH}_2 \cdot \text{CO} \cdot \text{NEt}_2$, when heated at 100° , gave the following numbers.

<i>t.</i>	Titre.	Urea present.
0	25.0	0.1000
60	19.15	0.0766
90	18.35	0.0734
170	17.7	0.0708
200	16.7	0.0668
260	16.7	0.0668

After three hours heating, the solution had acquired a faint ammoniacal smell and was alkaline to litmus paper. A very slight precipitate was obtained on the addition of calcium nitrate. The point of equilibrium in this case is much further removed from the urea end than in any of those previously considered, one-third of the urea having undergone transformation into diethylammonium cyanate. Calculating K from $\xi = 0.0668$ we obtain $K = \frac{0.0332^2}{0.0668} = 0.0165$.

For the direct transformation of decinormal diethylammonium cyanate at 59.6° , the following values were obtained.

<i>t.</i>	Titre.	<i>x.</i>	<i>k.</i>
20	3.7	0.0148	0.088
35	5.8	0.0232	0.089
55	7.8	0.0312	0.087
80	9.8	0.0392	0.088
110	11.9	0.0476	0.097
Mean.....			0.090

The value of k' is $Kk = 0.0165 \times 0.090 = 0.00148$.

Whilst the constant for the direct transformation of the cyanate is not greatly different from the constant for the monethylammonium compound, namely 0.081, the constant of the reverse action is twenty times greater than the corresponding constant for monethyl urea, in consequence of the very different positions of the points of equilibrium in the two cases.

Dimethylammonium Cyanate.

A decinormal solution of unsymmetrical dimethylurea gave the following numbers on heating at 100°.

<i>t.</i>	Titre.	Urea present.
0	25·0	0·1000
30	23·8	0·0952
60	23·4	0·0936
90	22·8	0·0912
150	21·6	0·0864
210	21·1	0·0844
270	21·1	0·0844

After three hours heating, the solution had a feeble ammoniacal smell and gave no precipitate with calcium nitrate; after five hours the ammoniacal odour had greatly increased in intensity, and a slight turbidity with calcium nitrate was observed. The value of ξ is 0·0844, from which we obtain $K = \frac{0·0156^2}{0·0844} = 0·00288$.

The following table contains the results of the transformation of a decinormal solution of dimethylammonium cyanate at 59·6°.

<i>t.</i>	Titre.	<i>x.</i>	<i>k.</i>
20	8·2	0·0328	0·242
35	11·8	0·0472	0·260
45	13·0	0·0520	0·248
55	14·3	0·0572	0·253
75	16·2	0·0648	0·262
Mean.....			0·253

For k' we have $Kk = 0·00288 \times 0·253 = 0·00073$.

Here the rate of the direct transformation is almost double that found for the monomethyl compound, and is indeed the greatest we have observed. The constant for the reverse action is no less than thirty times greater than that for the transformation of monomethylurea, but is still much less than the corresponding constant for unsymmetrical diethylurea.

Isoamylammonium Cyanate, $\text{NH}_3(\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2)\text{CNO}$.

The urea prepared from this amylammonium cyanate melted at 88—89°, the melting point given by Custer (*Ber.*, 1879, 12, 1330) being 89—91°. A decinormal solution yielded the following results at 100°.

<i>t.</i>	Titre.	Urea present.
0	25.0	0.1000
30	24.8	0.0992
90	24.3	0.0972
180	23.65	0.0946
270	23.6	0.0944

After five hours heating, the solution of the urea was slightly coloured, but had no ammoniacal smell, and gave no precipitate with calcium nitrate solution. The value of ξ being 0.0944, we have

$$K = \frac{0.0056^2}{0.0944} = 0.000334.$$

The results obtained for the transformation of the amylammonium cyanate at 59.6° were as follows.

<i>t.</i>	Titre.	<i>x.</i>	<i>k.</i>
40	7.2	0.0288	0.090
70	10.5	0.0420	0.100
100	12.1	0.0484	0.089
130	13.7	0.0548	0.090
175	15.6	0.0624	0.093
235	17.1	0.0684	0.090

Mean..... 0.092

For k' we obtain $Kk = 0.000334 \times 0.092 = 0.000031$.

The constants in this case resemble more closely those of the monethyl compounds than the constants of any of the other alkyl derivatives we have investigated.

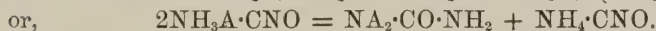
Tertiary Amylammonium Cyanate, $\text{NH}_3(\text{CMe}_2\text{Et})\cdot\text{CNO}$.

Tertiary amylurea, melting at 155°, exhibited an abnormal behaviour when heated in decinormal aqueous solution at 100°. The titre, which at first diminished, after an interval of three hours reached a minimum, and then increased as the heating was prolonged.

<i>t.</i>	Titre.	Urea present.
30	21.1	0.0844
60	17.95	0.0718
90	16.2	0.0648
120	15.5	0.0620
150	14.8	0.0592
180	14.3	0.0572
200	15.1	0.0602?
230	15.5	0.0620?

The solution had acquired a pronounced ammoniacal smell after 90 minutes heating, and, after two hours, gave a very slight pre-

precipitate with calcium nitrate. When the minimum titre was reached, a light precipitate consisting of slender interlaced needles was observed to have separated from the solution, and this increased in bulk as the heating was continued. A small quantity of a white sublimate of similar appearance was also formed in the coldest part of the tube above the solution. Wurtz who first prepared tertiary amylurea (pseudo-amyleneurea) states that when tertiary amylammonium cyanate is treated with caustic potash it is converted into unsymmetrical tertiary diamylurea (pseudo-diamyleneurea; *Annalen*, 1866, **139**, 330). This substance he describes as being almost insoluble in water and extremely volatile, subliming to a network of light delicate needles. Its properties are, therefore, identical with those of the substance observed by us, which was probably formed according to the equations



The ammonium cyanate, supposed to be produced in the second equation, might either appear as urea or as ammonium carbonate, more probably as the latter, as the rise in the titre would then be accounted for (compare Walker and Hambly, *loc. cit.*, 750). The abnormal course of the transformation renders the end-point uncertain, but the minimum value 0.0572 may be taken as an approximate value of ξ , an almost identical number having been obtained when the urea was transformed at 79.6°.

Tertiary amylammonium chloride was prepared from the corresponding urea as follows. The urea was boiled with strong potash solution for several hours in a flask with condensing tube, so that the ammonia might escape, and the amylamine be returned to the flask. The contents were next distilled into hydrochloric acid solution, and the solution of chlorides thus obtained evaporated almost to dryness on the water bath; the evaporation was completed in an exhausted desiccator over solid potash. Very little ammonium chloride was present, for on the conversion of a portion of the chloride into cyanate in the usual way, by means of silver cyanate, and rapid evaporation to dryness of the cyanate solution, the urea obtained melted at 155°, the melting point of the original substance.

A decinormal solution of the amylammonium cyanate, prepared in the manner above indicated, was heated at 59.6° with the following result.

<i>t.</i>	Titre.	<i>x.</i>	<i>k.</i>
100	3.0	0.0120	0.0137
160	4.1	0.0164	0.0127
220	4.4	0.0176	0.0101
404	6.1	0.0244	0.0085
584	7.6	0.0304	0.0082

The magnitude k was calculated with the end-point $\xi = 0.0572$, whence $K = \frac{0.0428^2}{0.0572} = 0.032$. It will be seen that the value does not remain constant, but continually diminishes as the action proceeds; this is no doubt due to secondary decompositions of the same nature as those undergone by the urea. Wurtz remarks (*loc. cit.*, p. 329) that tertiary amylurea exhibits a marked tendency to break up, with the formation of amylene as one of the products of decomposition. At the beginning of the action, the values of k are probably nearest the true value, so that we may adopt $k = 0.013$ as being approximately correct. A second set of experiments yielded almost identical results, the value of k for the first two determinations being 0.0135.

For k' we have $Kk = 0.032 \times 0.013 = 0.0004$.

Although these values for k and k' are somewhat uncertain, they are sufficiently accurate to show that whilst the direct transformation proceeds much more slowly than is the case with any of the other compounds examined, the reverse transformation is only exceeded in velocity by the diethyl and dimethyl compounds.

Comparison of Constants.

In the following table the values of the constants for the various cyanates and ureas have been collected, in order to exhibit any regularities that might exist amongst them.

Cyanate.	100 <i>k</i> .	100 <i>k'</i> .
Ammonium.....	14.4	0.0038
Methylammonium.....	13.4	0.0022
Dimethylammonium.....	25.3	0.073
Ethylammonium.....	8.1	0.007
Diethylammonium.....	9.0	0.148
Isoamylammonium.....	9.2	0.0031
Tertiary amylammonium...	1.3	0.04

The values of the constants have all been multiplied by 100 to avoid unnecessary ciphers, and to give the results in percentages. Thus in the case of ammonium cyanate the numbers indicate that in a normal solution 14.4 per cent. would be transformed in the first minute if the concentration were maintained constant, the corresponding amount of retransformation in a normal solution of urea being only 0.0038 per cent. It must be borne in mind, however, that these values of k and k' would not agree exactly with those obtained by actual experiment in normal solutions, for in calculating them the change of dissociation effected by dilution has been neglected, and it has been shown by Walker and Hambly (*loc. cit.*, 763) that neglect

of this factor gives greater values for k in dilute solutions than it does in more concentrated solutions.

A glance at the table suffices to show that there is no pronounced regularity in the values of k . The introduction of a methyl group into ammonium cyanate leaves the velocity constant practically unaffected; a second methyl group, however, raises it to almost double the original value. Ethyl groups diminish the value of the constant, the diminution being somewhat greater for the introduction of one group than for two. The increase in the constant effected by the second ethyl group is, however, very slight, and not at all comparable with the effect of a second methyl group. Both the amyl radicles lower the constant, the lowering in the case of tertiary amyl being very marked. The isomeric ethylammonium cyanate and dimethylammonium cyanate have very different constants. This might be attributed to the fact that one isomeride is the salt of a primary base whilst the other is a salt of a secondary base, but the widely divergent values of the amylammonium cyanates, where both bases are primary, show that isomerism within the alkyl group has as marked an influence on the constant as isomerism directly affecting the nitrogen atom.

The values of k' display as little regularity as the values of k . The introduction of one alkyl group into urea sometimes raises and sometimes lowers the constant; the introduction of a second alkyl group increases the value greatly in both cases examined. Isomeric substances again have very different values of the constant.

Points of Equilibrium.

In calculating k and k' for 59.6° , use was made of the end-point ξ , determined at 100° . The calculation thus proceeds on the assumption that the end-point is not appreciably influenced by temperature. This has already been shown to be the case for ammonium cyanate (*loc. cit.*, 751), but there the circumstances were unfavourable for detecting any small variation. In the case of diethylurea and tertiary amylurea, the reverse action proceeds with considerable rapidity, and the equilibrium point is at a considerable distance from either end, so that the conditions are favourable for observing any displacement of this point by temperature. Experiments were therefore made at 80° with both of these substances, with the result that the end-points observed at that temperature were, within the experimental error, identical with those obtained at 100° . Temperature, then, influences the position of the end-point to so small a degree that it is permissible to use the point of equilibrium determined at one temperature in calculating the velocity constants for another.

The point of equilibrium is greatly influenced by the concentration

of the solution, as the following consideration will show. The transformation of a cyanate into the corresponding urea is a bimolecular action; the reverse transformation of urea into cyanate is a unimolecular action. In the latter case, each molecule is transformed independently of the others, so that the proportion of the whole transformed in a given time is quite independent of the dilution. On the other hand, two ions must meet before a molecule of urea can be formed; consequently a smaller proportion of cyanate will be converted into urea as the dilution increases, for the chance of the ions meeting varies as the inverse square of the dilution. The result is that as the solutions are taken more and more dilute, the greater will be the proportion of ammonium cyanate present when equilibrium has been attained. It is easy to calculate the dilution at which half the cyanate has been converted into urea when equilibrium has been reached by means of the equation

$$K = \frac{(A - \xi)^2}{\xi}.$$

If we express A , the original concentration in terms of a normal solution, and ξ in terms of A , we have the following equation for the case of equilibrium in which the transformation has gone half way,

$$K = \frac{(A - 0.5 A)^2}{0.5 A} = 0.5 A.$$

That is, the original concentration of cyanate expressed in terms of a normal solution for which the transformation into urea will stop half way is numerically equal to twice the ratio of the velocity constants, K , as determined from any single end-point experiment. The values of the end-points and of $2K$ for the various cyanates are tabulated below.

Cyanate.	100%.	2K.
Ammonium.....	95.0	0.00052-normal.
Methylammonium	96.0	0.00033
Dimethylammonium	84.4	0.0057
Ethylammonium.....	91.2	0.0017
Diethylammonium	66.8	0.033
Isoamylammonium	94.4	0.00067
Tertiary amylammonium.	57.0	0.064

In the first column the end-points are given in percentages for decinormal solutions; for example, the conversion of ammonium cyanate into urea ceases when 95 per cent. of the original amount has been transformed. The numbers in the second column give the concentrations of the solutions in which the transformation will come to an end, when half the cyanate (or half the urea) has disappeared. It

should again be remarked that owing to neglect of the influence of dilution on the degree of electrolytic dissociation, these numbers are somewhat greater than the true values, the error being relatively larger the smaller the number is. The table, therefore, rather under-rates the differences between the various substances. A solution of methylurea has consequently to be diluted more than 200 times as far as a solution of tertiary amylurea in order to get the same amount of urea decomposed in both cases.

Trialkyl- and Tetraalkyl-ammonium Cyanates.

Although trialkyl- and tetraalkyl-ammonium cyanates are not supposed to be transformed into ureas by heating with water, a few experiments were made with them in decinormal aqueous solution, in order to ascertain their behaviour under conditions similar to those with the monalkyl- and dialkyl-ammonium cyanates.

Tetramethylammonium cyanate, prepared from the iodide and silver cyanate, did not change in titre after heating for 18 hours at 59.6° . Triethylammonium cyanate, on the other hand, exhibited distinct signs of change, even after one hour's heating, as may be seen from the following table.

<i>t.</i>	Titre.
30	0.1
90	0.2
150	0.25
1320	1.00
2700	1.85

When the experiment was interrupted, the solution was found to be strongly ammoniacal, and to give a copious precipitate with calcium nitrate. Five c.c. of the solution at $t = 2700$ were treated with excess of calcium nitrate, and the precipitate filtered off. To the filtrate 5 c.c. of decinormal silver nitrate solution were added, and the insoluble salt so obtained was then removed by filtration. The titre of the filtrate was now found to be 12.0 c.c. instead of 1.85, the number obtained without treatment with calcium nitrate. These figures would seem to indicate that the final product of the transformation in this case is mostly acid triethylammonium carbonate, produced from the normal carbonate by protracted heating.

XXII — *Luteolin*. Part I.

By ARTHUR G. PERKIN, F.R.S.E.

THE yellow dyestuff weld, which contains the colouring matter luteolin, is the dried herbaceous plant known as *Reseda luteola*, a native of Europe, formerly cultivated in many parts, especially in France and Germany. Although with tin and aluminium mordants it yields purer and faster yellow shades than those given by quercitron and other well known natural dyestuffs, it is now but little employed, chiefly on account of the small amount of colouring matter it contains.

In continuation of the study of the action of acids on the natural yellow colouring matters (Trans., 1895, **67**, 644), it was desirable to test the behaviour of luteolin in this respect, and being then struck by the very meagre examination it had received, it was deemed advisable to subject it to further investigation.

Luteolin was isolated from weld by Chevreul (*J. Chim. méd.*, **6**, 157), and subsequently studied by Moldenhauer (*Annalen*, 1856, **100**, 180), who assigned to it the formula $C_{20}H_{14}O_8$. Schützenberger and Paraf (*Jahresbericht*, 1861, 707), on the other hand, considered it to have the formula $C_{12}H_8O_5$, and describe a lead salt, $PbO, C_{12}H_8O_5$. Somewhat later Hlasiwetz and Pfaundler (*Annalen*, 1859, **112**, 107) gave it the formula $C_{15}H_{10}O_6$, which is isomeric with paradiscetin, a substance they obtained by the action of fused alkali on quercetin (*Annalen*, 1859, **112**, 102). By the action of nitric acid on luteolin, Rochleder (*Zeit. für Chem.*, 1886, 602) obtained oxalic acid, and with fused alkali protocathechuic acid and a substance which he considered was in all probability phloroglucin. According to Chevreul (*loc. cit.*), luteolin unites with acids.

EXPERIMENTAL PART.

The preliminary experiments on the preparation of luteolin were carried out according to Moldenhauer's directions (*loc. cit.*), but as the results were somewhat unsatisfactory, a new method was devised. Owing to the small amount of colouring matter which weld contains, the extraction of luteolin from the plant itself had to be abandoned, a commercial extract of the dyestuff being found preferable. For this purpose, however, it was necessary to have an extract specially prepared for this investigation, for experience showed that many of the so-called "weld" extracts in the market are not preparations of weld at all; owing to ignorance of this fact, much time and

labour was lost, some of the so-called "weld" extracts being found to consist chiefly of extract of Persian berries.

Three hundred grams of true weld extract, dissolved in 3 litres of water to which 100 c.c. of hydrochloric acid was added, was digested at a boiling heat for several hours; the liquid was at first opaque, but as the boiling proceeded, a black, tarry mass gradually separated, and, as soon as this ceased to form, it was removed by filtration through calico, and the clear filtrate allowed to stand for 12 hours. The brown amorphous precipitate of impure luteolin which had then separated was collected, and, after being washed with water, was suspended in the same liquid, and shaken up with a large volume of ether, in which most of it dissolved. As the ethereal liquid did not always readily separate from the mixture, it was found preferable to strain the whole through calico, separation quickly taking place when the undissolved product had been removed. The ethereal solution was now extracted with dilute alkali, the alkaline extract neutralised with acid, and the yellow precipitate collected, washed with water, and allowed to drain upon a porous tile until it had the consistency of a thin clay. A saturated solution of this product in boiling alcohol, on cooling, deposited a crystalline mass, which was collected and repeatedly recrystallised from dilute alcohol until pure.

As the residue left undissolved by the ether during the purification of the crude luteolin still contained some colouring matter, it was dissolved in a little alcohol, the solution treated with a large volume of ether, filtered, and the filtrate washed with water; from this, by extraction with alkali and treatment as above, pure luteolin could be obtained. The black, tarry matter which separated during the boiling of weld extract with dilute acid contained but a mere trace of colouring matter. An analysis of luteolin dried at 160° gave the following result.

0.1149 gave 0.2644 CO_2 and 0.0413 H_2O .	$\text{C} = 62.75$; $\text{H} = 3.99$ p.c.
$\text{C}_{12}\text{H}_8\text{O}_5$ (Schützenberger and Paraf) requires	$\text{C} = 62.07$; $\text{H} = 3.44$ „
$\text{C}_{15}\text{H}_{10}\text{O}_6$ (Hlasiwetz and Pfaundler)	„ $\text{C} = 62.94$; $\text{H} = 3.49$ „
$\text{C}_{20}\text{H}_{14}\text{O}_8$ (Moldenhauer)	„ $\text{C} = 62.82$; $\text{H} = 3.66$ „

This result, therefore, agrees well with the formulæ $\text{C}_{15}\text{H}_{10}\text{O}_6$ and $\text{C}_{20}\text{H}_{14}\text{O}_8$, but not with the formula $\text{C}_{12}\text{H}_8\text{O}_5$.

In conjunction with L. Pate (Trans., 1895, **67**, 644), I have previously shown that quercetin, fisetin, and various other allied yellow colouring matters, yield peculiar compounds with mineral acids, which as a rule indicate the molecular weight of these substances. The behaviour of luteolin towards these acids was therefore studied.

Luteolin Sulphate.—The addition of sulphuric acid to a saturated solution of luteolin in boiling acetic acid caused the formation of an

orange-coloured liquid, from which crystals gradually deposited on cooling. These were collected, washed with acetic acid, and dried.

0.1229 gave 0.2104 CO_2 and 0.0378 H_2O . $\text{C} = 46.69$; $\text{H} = 3.41$.

0.1534 „ 0.2635 „ „ 0.0475 „ $\text{C} = 46.84$; $\text{H} = 3.44$.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{H}_2\text{SO}_4$ requires $\text{C} = 46.87$; $\text{H} = 3.12$ per cent.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{H}_2\text{SO}_4$ „ $\text{C} = 50.00$; $\text{H} = 3.33$ „

The compound consisted of a mass of orange-red needles, insoluble in acetic acid; by treatment with water it is decomposed quantitatively into luteolin and sulphuric acid, as the following result shows.

0.5225 gave 0.3910 $\text{C}_{15}\text{H}_{10}\text{O}_6$ and 0.3174 BaSO_4 . $\text{C}_{15}\text{H}_{10}\text{O}_6 = 74.81$; $\text{S} = 8.35$.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{H}_2\text{SO}_4$ requires $\text{C}_{15}\text{H}_{10}\text{O}_6 = 74.48$; $\text{S} = 8.33$ per cent.

Luteolin Hydrobromide.—When hydrobromic acid is added to a pasty mixture of luteolin with boiling acetic acid, a clear solution is formed, but crystals are not deposited on cooling, unless a considerable excess of the acid has been used. The product thus obtained was washed with acetic acid and dried.

0.1250 gave 0.2160 CO_2 and 0.0375 H_2O . $\text{C} = 47.12$; $\text{H} = 3.33$.

0.1331 „ 0.2298 „ „ 0.0435 „ $\text{C} = 47.09$; $\text{H} = 3.63$.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HBr}$ requires $\text{C} = 49.04$; $\text{H} = 3.00$ per cent.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HBr}, \text{H}_2\text{O}$ requires $\text{C} = 46.75$; $\text{H} = 3.37$ per cent.

It consisted of an ochre-coloured mass of fine needles, which, by contact with water, are somewhat slowly decomposed into luteolin and hydrobromic acid, being much more stable in this respect than the corresponding compounds of quercetin, fisetin, and morin (*loc. cit.*).

0.4124 gave 0.3081 $\text{C}_{15}\text{H}_{10}\text{O}_6$. $\text{C}_{15}\text{H}_{10}\text{O}_6 = 74.70$.

0.6267 „ 0.4690 „ and 0.3040 AgBr . $\text{C}_{15}\text{H}_{10}\text{O}_6 = 74.81$; $\text{Br} = 20.63$.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HBr}, \text{H}_2\text{O}$ requires $\text{C}_{15}\text{H}_{10}\text{O}_6 = 73.93$; $\text{Br} = 20.67$ per cent.

To be certain that the product obtained on decomposing the hydrobromide by means of water was luteolin, it was dried at 160° and analysed, with the following result.

0.1214 gave 0.2800 CO_2 and 0.0397 H_2O . $\text{C} = 62.90$; $\text{H} = 3.63$.

$\text{C}_{15}\text{H}_{10}\text{O}_6$ requires $\text{C} = 62.94$; $\text{H} = 3.49$ per cent.

Luteolin hydrochloride was prepared in the same way as the hydrobromide, which it closely resembles.

0.1384 gave 0.2675 CO_2 and 0.0472 H_2O . $\text{C} = 52.71$; $\text{H} = 3.79$.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HCl}$ requires $\text{C} = 55.81$; $\text{H} = 3.41$ per cent.

$\text{C}_{15}\text{H}_{10}\text{O}_6, \text{HCl}, \text{H}_2\text{O}$ requires $\text{C} = 52.86$; $\text{H} = 3.81$ per cent.

Luteolin hydriodide crystallises beautifully in orange-coloured glistening prisms. It was not analysed.

The sulphuric acid compound of luteolin is of the normal character, and shows that the true formula of luteolin is $C_{15}H_{10}O_6$. The compounds of luteolin with the haloid acids are, however, peculiar, in that they appear to crystallise with $1H_2O$, and differ in this respect from the corresponding compounds of quercetin, fisetin, and morin, which do not contain water of crystallisation. Attempts to remove the water were ineffectual, the weight of these compounds remaining constant even at the temperature of boiling aniline, but the supposition that they contain water of crystallisation receives weight from their comparative stability towards water, and the fact that they are not formed except in the presence of some quantity of the aqueous acid. Moreover, analysis has shown that the formula of luteolin cannot be $C_{15}H_{10}O_6 + H_2O$ ($C_{15}H_{12}O_7$) ($C = 59.21$; $H = 3.94$); and further, luteolin is regenerated from them by prolonged contact with water. They must therefore possess the formula assigned to them.

Dibromoluteolin.—In order to leave not the slightest doubt as to the molecular weight of luteolin, experiments were carried out with the object of preparing a bromine derivative. Luteolin ground into a thin paste with acetic acid was treated with slightly more than the theoretical amount of bromine necessary for the production of a dibromo-derivative. Hydrogen bromide was evolved, and after the mixture had been left for 48 hours, the product was drained upon a porous tile, and purified by crystallisation from acetic acid.

0.1339 gave 0.2000 CO_2 and 0.0300 H_2O . $C = 40.73$; $H = 2.48$.

0.3061 „ by Carius' method 0.2610 $AgBr$. $Br = 36.29$.

$C_{15}H_8Br_2O_6$ requires $C = 40.54$; $H = 1.80$; $Br = 36.04$ per cent.

There can, therefore, be no doubt that the formula of luteolin is correctly represented by $C_{15}H_{10}O_6$.

Dibromoluteolin was obtained as a glistening mass of lemon-yellow needles, melting at 303° , sparingly soluble in alcohol, and acetic acid.

By crystallisation from dilute alcohol, luteolin is obtained as a glistening mass of yellow needles almost identical in appearance with quercetin or fisetin. Examined in Zeisel's apparatus, it was found to contain no methoxy-group. As previously shown by other workers it melts above 320° , and yields with ferric chloride in alcoholic solution first a green, and then a brown-red, coloration.

Tetracetyluteolin.—A solution of one part of luteolin, and one of anhydrous sodium acetate in six parts of acetic anhydride was boiled for one hour, the product poured into water, and after being allowed

to stand 24 hours, collected and purified by crystallisation from alcohol.

0.1108 gave 0.2465 CO_2 and 0.0399 H_2O . $\text{C} = 60.67$; $\text{H} = 4.00$.

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$ requires $\text{C} = 60.79$; $\text{H} = 3.96$ per cent.

It forms a silky mass of colourless needles melting at $213-215^\circ$, very sparingly soluble in alcohol. It is insoluble in cold alkaline solutions.

In order to determine the number of acetyl groups present, a slight modification of Liebermann's method was adopted. To a solution of the substance in boiling acetic acid, a few drops of sulphuric acid were added and the whole boiled for about a minute; a considerable quantity of boiling water was then added, and the crystals of luteolin which separated on cooling, were collected and weighed.

0.5283 gave 0.3310 luteolin. $\text{C}_{15}\text{H}_{10}\text{O}_6 = 62.65$.

$\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_2\text{H}_3\text{O})_3$ requires $\text{C}_{15}\text{H}_{10}\text{O}_6 = 69.41$ per cent.

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_2\text{H}_3\text{O})_4$ „ $\text{C}_{15}\text{H}_{10}\text{O}_6 = 62.99$ „

It was, therefore, a *tetracetyl* derivative.

Dibromotetracetyl luteolin, prepared from dibromoluteolin in a similar way to the above compound from luteolin, was obtained in the form of fine colourless needles melting at $218-220^\circ$; it is very sparingly soluble in alcohol.

0.1359 gave 0.2220 CO_2 and 0.0353 H_2O . $\text{C} = 44.62$; $\text{H} = 2.88$.

$\text{C}_{15}\text{H}_4\text{O}_6\text{Br}_2(\text{C}_2\text{H}_3\text{O})_4$ requires $\text{C} = 45.09$; $\text{H} = 2.61$ per cent.

Tetrabenzoyl luteolin was prepared from luteolin by the method of Baumann and Schotten, using a ten per cent. solution of caustic soda. The colourless sticky product thus formed became solid after some hours; it was then ground into a paste with water, well washed with dilute alkali, and purified by crystallisation from benzene.

0.1114 gave 0.2996 CO_2 and 0.0397 H_2O . $\text{C} = 73.33$; $\text{H} = 3.95$.

$\text{C}_{15}\text{H}_7\text{O}_6(\text{C}_7\text{H}_5\text{O})_3$ requires $\text{C} = 72.24$; $\text{H} = 3.65$ per cent.

$\text{C}_{15}\text{H}_6\text{O}_6(\text{C}_7\text{H}_5\text{O})_4$ „ $\text{C} = 73.50$; $\text{H} = 3.70$ „

It was, therefore, a *tetrabenzoyl* derivative. From benzene, in which it is sparingly soluble, it was obtained as a spongy mass of colourless needles melting at $200-201^\circ$.

Action of Fused Alkali on Luteolin.—Rochleder (*loc. cit.*) has stated that luteolin, when fused with alkali, yields protocathecinic acid, and probably phloroglucin, but as judging from the formula of luteolin the production of the latter seemed somewhat unlikely, experiments were made to determine this point. Unfortunately, however, but a small quantity of pure luteolin was available for this purpose, and the results obtained, although sufficient to prove that phloro-

glucin is not produced at the temperature employed, must be considered as but preliminary to an exhaustive study of this reaction.

Luteolin was heated at 170—200° for half an hour with 10 times its weight of potassium hydroxide dissolved in a little water; the melt was dissolved in water, the solution neutralised with acid, extracted with ether, the extract evaporated, and the crystalline residue dissolved in a little caustic potash. After saturation with carbonic anhydride, the alkaline liquid was extracted with ether, and the residue left on evaporating the ethereal extract was purified by crystallisation from water. The mass of almost colourless needles thus obtained, melted at 210°, and when dissolved in water, the solution gave *no* coloration with ferric chloride. It could not, therefore, be phloroglucin, which gives such a characteristic reaction with this reagent. The further examination of this substance will no doubt throw considerable light on the constitution of luteolin.

To isolate the second product of the reaction, the remaining alkaline solution was neutralised with acid and extracted with ether; on evaporating the ethereal extract, a crystalline residue was obtained which after crystallisation from water, formed colourless needles melting at 195°; these, when dissolved in water, gave a strong green coloration with ferric chloride. It had all the properties of *protocatechuic acid* and was found to be identical with it.

Methylation of Luteolin.—One part of luteolin dissolved in a solution of 10 parts of caustic potash in methylic alcohol, was treated with excess of methylic iodide, and digested at the boiling heat for 24 hours. After removal of the excess of methylic iodide, and the greater portion of the alcohol by distillation, the residue was poured into water, the precipitated product dissolved in ether, and the resulting solution after being washed with dilute alkali was evaporated to a small bulk. The crystalline mass which separated on cooling, was collected, rinsed with a little ether, and purified by crystallisation from alcohol.

0.1078 gave 0.2643 CO₂ and 0.0555 H₂O. C = 66.86; H = 5.71.

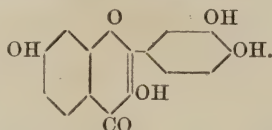
0.1264 „ 0.3102 CO₂ and 0.0635 H₂O. C = 66.92; H = 5.58.

C₁₅H₆O₆(CH₃)₄ requires C = 66.66; H = 5.55 per cent.

This compound is deposited from alcohol as a spongy mass of needles, of a faintly yellowish tint, insoluble in alkalis, and melting at 191—192°. A determination of the methoxy-groups present indicated that the compound contained but three of them, in which case it would be a derivative of methyl luteolin. Owing, however, to lack of material, this result cannot at present be confirmed, but it is hoped soon to be able to thoroughly investigate this reaction.

If the properties of luteolin be considered, one cannot but be

struck with their close similarity to those of fisetin, $C_{15}H_{10}O_6$, the colouring matter of "Young Fustic" (*Rhus Cotinus*, L.). This substance according to the investigations of Schmid (*Ber.*, 1886, **19**, 1739) and Herzig (*Ber.*, 1895, **28**, 293) contains four hydroxyl groups, yields a dibromo-derivative, is readily decomposed into resorcinol and protocathechuic acid, and, as I have shown (*loc. cit.*), also unites with mineral acids. Fisetin (Herzig, *loc. cit.*, and Kostanecki, *Ber.*, 1895, **28**, 2302) is most probably a tetrahydroxy- β -phenylpheno- γ -pyrone, and its constitution is as follows.



Though it is at present too early to speak with certainty as to the constitution of luteolin, it is most probable that its further examination will show it to differ only from fisetin in the position of the hydroxyl group in the pheno- γ -pyrone ring.

The study of luteolin will be continued by the author in conjunction with Mr. G. Y. Allen.

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XXIII.—*Lead Tetracetate and the Plumbic Salts.*

By A. HUTCHINSON, M.A., Ph.D., and W. POLLARD, B.A., Ph.D.

Introduction.

IN a note published in this Journal in September, 1893 (*Trans.*, 1893, **63**, 1136), we pointed out that the crystals obtained when minium is dissolved in glacial acetic acid were to be regarded as lead tetracetate, a salt of lead dioxide, and that it would in all probability be possible to prepare other salts of quadrivalent lead from this substance. During the past two years we have, as opportunity offered, attempted a fuller study of the properties of this compound, and, although some points are still under investigation, we venture now to lay before the Society the results we have so far obtained.

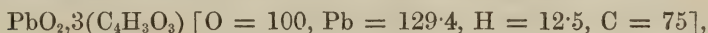
Lead Tetracetate.

Historical.—Since the time of Berzelius, chemists have been aware that minium is soluble in acetic acid, and a method of detecting and estimating certain impurities found in the commercial article has

been based on this fact. Little, however, was known of the properties of this solution till Jacquelin noticed (*Comptes rendus mensuels des Travaux Chimiques*, 1851, 1; *Abstr., J. pr. Chem.*, 1851, 53, 151), as Dumas had done before him, that a solution of minium in aqueous acetic acid soon decomposed and deposited lead dioxide; he found, also, that this decomposition was greatly accelerated by heat or by the addition of water, and further observed that when he employed glacial acetic acid at 40° as the solvent, the solution, on cooling, deposited a crop of slender, colourless, oblique prisms. The formation of these crystals had, Jacquelin tells us, been previously noted by Balard, who did not, however, study them.

A few years later, Schönbein (*J. pr. Chem.*, 1858, 74, 315) made similar observations on the behaviour of the solution of minium in acetic acid, and found that sulphuric acid precipitated only a part of the lead from this liquid, leaving in solution the "acetate of lead peroxide;" Schönbein does not appear to have been acquainted with Jacquelin's work, nor to have obtained any crystals from his solutions. On filtering off the crystals of "acétate de bioxide de plomb," and attempting to dry them between filter paper, Jacquelin found that they quickly turned brown, decomposing into lead peroxide and acetic acid. On the addition of water, this decomposition became complete, and he was therefore able to determine the percentage of acetic anhydride in the substance by titrating the aqueous solution with standard alkali. The lead was estimated as chloride in another portion.

The results led him to adopt the improbable formula



which requires lead dioxide = 43.86 and acetic anhydride = 56.14 per cent. Finding that Jacquelin's improbable formula was based on insufficient data, we determined to submit the substance anew to investigation.

Preparation.—Commercial red lead was added little by little to hot glacial acetic acid till no more dissolved and lead peroxide began to separate; the solution was then either filtered hot, or the crystals deposited on cooling were subsequently freed from peroxide by collecting them in a funnel on a porcelain filtering plate, and washing away the finely divided peroxide by cold acetic acid. The crystals were purified by recrystallisation from hot glacial acetic acid, and dried over sulphuric acid in a vacuum.

As regards the interaction which takes place, Jacquelin seems to have held the view that a compound of minium with acetic acid is first formed, for he speaks of an "acetate of minium" which, as the solution crystallises, splits up, yielding crystals of acetate of

dioxide of lead, and ordinary lead acetate which remains dissolved. Schönbein, on the other hand, believed that when minium dissolved in acetic acid, the two oxides contained in the former separated, and that both lead acetate and acetate of the peroxide were present in solution. As, however, lead peroxide is insoluble in acetic acid, Schönbein adopted the hypothesis that lead peroxide can exist in two conditions, in one of which it is capable of union with acetic acid and in the other incapable of such combination.

We are inclined to think that Schönbein's view is in the main the correct one, for it is conceivable that the peroxide set free from minium by abstraction of lead monoxide should, at the moment of its formation, be capable of combining with acetic acid, although it is insoluble when once formed. We have not, however, so far been able to obtain fresh direct experimental evidence bearing on this point.

The substance can be readily analysed by taking advantage of the extraordinary ease with which water decomposes it; a weighed portion was treated with hot water, the PbO_2 collected on a tared filter, dried at 110° , and weighed, the acetic acid being estimated in the filtrate by titration with a standard alkali. The lead determinations were checked by direct conversion of other portions into chloride and sulphate by evaporation with the respective acids.

Analyses I, II, and IV were made on different samples, II and III on the same.

- I. 0.8757 gave 0.4735 PbO_2 , and required 98.4 c.c. of potash solution (1 c.c. = 0.00448 KOH).
 II. 0.8770 gave 0.4755 PbO_2 , and required 79.9 c.c. of soda solution (1 c.c. = 0.00395 NaOH).
 III. 0.6403 gave 0.4040 PbCl_2 .
 IV. 0.5474 gave 0.3760 PbSO_4 .

	I.	II.	III.	IV.	Calculated for $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$.
PbO_2	54.07	54.22	54.26	54.16	53.93
$(\text{CH}_3\text{CO})_2\text{O}..$	45.85	45.88	—	—	46.07
	<hr/> 99.92	<hr/> 100.10			<hr/> 100.00

The pure crystals begin to melt at 175° , and decompose at a temperature a few degrees higher. The only substance known to us which dissolves the tetracetate without change is glacial acetic acid, in which it is readily soluble when hot, crystallising out again on cooling. Before using this solvent for the molecular weight determinations, we estimated the amount of tetracetate contained in a solution saturated at 17° . For this purpose, two portions of the solution were weighed, and the lead determined in the one case as chloride, and in the other as sulphate.

- I. 10.57 grams of solution gave 0.178 of PbCl_2 . Hence 100 grams of acetic acid dissolve 2.76 grams of lead tetracetate at 17° .
- II. 10.57 grams of solution gave 0.1947 gram of PbSO_4 . Hence 100 grams of acetic acid dissolve 2.77 grams of lead tetracetate at 17° .

Lead tetracetate is easily soluble in cold chloroform, but, owing to partial decomposition, gives a muddy-brown solution. If, however, the acetate is previously moistened with a small quantity of acetic acid a clear solution is obtained. Boiling carbon tetrachloride (dried over fused calcium chloride or over phosphoric anhydride) dissolves it slightly, the greater part of the salt crystallising out on cooling. Hot benzene (dried over sodium) dissolves it somewhat more readily; in both these cases a small quantity of acetic acid is necessary to prevent the solution turning brown. The tetracetate is very slightly soluble in ether and light petroleum, and only slowly attacked by these solvents if they are thoroughly dry.

The specific gravity was determined in a pycnometer in the ordinary way, but, owing to the difficulty of finding any other liquid which would neither dissolve nor act on the salt we were obliged to use a saturated solution of the tetracetate in glacial acetic acid.

The specific gravity of the solution saturated at 16.4 was 1.0692 at $16.4/4^\circ$.

A second determination made as a control, in a small pycnometer, on a portion of the solution which had just been used for finding the specific gravity of the solid gave the value 1.0678 at $17.2/4^\circ$.

Two determinations of the specific gravity of the solid as compared with the solution gave the values 2.084 at 16.9° and 2.075 at 18.2° . Hence the specific gravity of the solid, as compared with water at 4° , is (A) 2.228 at 16.9° and (B) 2.218 at 18.2° ; of these results, A is probably the more accurate, and was got by using 8.484 grams of the solid in a 25 c.c. pycnometer, especial care being taken to get rid of all air bubbles.

Crystallography of Lead Tetracetate.

The crystals are typically monoclinic, colourless, transparent prisms, greatly elongated in the direction of the c axis. They are usually 10 to 25 mm. in length, and 1 to 2×1 to 2 mm. in section.

The faces m and b are often about equally developed, their combination giving a nearly hexagonal prism. The form $n\{210\}$ is not of very frequent occurrence, and is always narrow and subordinate. Cleavage b perfect.

The crystals decomposed so easily that no complete optical examination could be made.

The extinction observed through b makes an angle of $-16\frac{1}{2}^\circ$ with

the c axis, and this is the direction of vibration of the ray traversing the plate with the greatest velocity.

System: Monoclinic.

Ratio of axes:

$$a : b : c = 0.5874 : 1 : 0.48485. \quad \beta = 74^\circ 24'.$$

Forms observed:

$$b = \{010\}, m = \{110\}, n = \{210\}, q = \{011\}.$$

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$mm''' = 110 : \bar{1}10$	8	$59^\circ 36' - 58^\circ 34'$	$59^\circ 0'$	$59^\circ 0'$
$mb = 110 : 010$	12	$60 17 - 60 47$	$60 30$	*
$nn''' = 210 : 2\bar{1}0$	2	$31 43 - 31 37$	$31 40$	$31 36$
$nb = 210 : 010$	6	$74 20 - 74 2$	$74 12$	$74 12$
$nm = 210 : 110$	5	$13 52 - 13 19$	$13 38$	$13 42$
$qq' = 011 : 0\bar{1}1$	4	$50 14 - 49 54$	$50 4$	$50 4$
$qb = 011 : 010$	11	$65 12 - 64 45$	$64 58$	*
$qin = 011 : \bar{1}10$	5	$90 20 - 90 3$	$90 13$	*
$qm' = 011 : 110$	1	—	$65 4$	$65 8$

Molecular Weight of Lead Tetracetate by Raoult's Methods.—The only solvent available for this purpose was glacial acetic acid; the specimen employed was carefully purified by recrystallisation, and melted at 16.58° .

The freezing-points of solutions of various concentrations were determined in Beckmann's apparatus (*Zeit. physikal. Chem.*, 1891, **7**, 323), and the precautions taken by him to prevent the acid absorbing moisture from the air, were found highly necessary, and were duly observed. The earlier boiling point determinations were made with Beckmann's original apparatus (*Zeit. physikal. Chem.*, 1889, **4**, 543); better results were, however, subsequently obtained with the improved form described by him in 1891 (*Zeit. physikal. Chem.*, 1891, **8**, 223). Preliminary experiments made by adding successive portions of acetate to the boiling solvent proved unsatisfactory, probably because a slight decomposition of the acetate was brought about either by the long-continued boiling of its solution, by the action of moisture, or by organic matter derived from the cork, and we found it advisable to eliminate as far as possible these sources of error by making a separate determination at each concentration. The constants of the acid were taken as 39 and 25.3 respectively. Our results are contained in the following tables.

The molecular weight of $Pb(C_2H_3O_2)_4$ is 443. The numbers tabulated on p. 217 leave but little doubt, therefore, that in solution lead tetracetate consists essentially of molecules of the formula $Pb(C_2H_3O_2)_4$.

Freezing Point Method.

Experi- ment.	Grams of solvent.	Grams of substance.	Rise observed.	Grams of substance in 100 of solvent.	Molecular weight.
I	26·2	0·1915	0·070	0·73	407·0
		0·4538	0·164	1·73	412·0
		0·5544	0·202	2·11	408·5
		0·6690	0·243	2·55	410·0
II	25·9	0·3616	0·138	1·40	394·5
		0·6513	0·238	2·52	412·0
III	25·0	0·1250	0·049	0·50	398·0

Boiling Point Method.

Experi- ment.	Grams of solvent.	Grams of substance.	Rise observed.	Grams of substance in 100 of solvent.	Molecular weight.
I	21·1	0·2578	0·087	1·02	355
II	50·4	0·5620	0·075	1·11	376
III	25·3	0·4830	0·132	1·91	366
IV	51·5	0·9950	0·134	1·93	365
V	52·4	1·2363	0·167	2·36	357
VI	26·5	1·4733	0·377	5·56	373
VII	23·9	2·0860	0·609	8·72	362

It is interesting in this connection to compare these numbers with the value 69 obtained by Beckmann for the mean molecular weight of sodium acetate dissolved in boiling glacial acetic acid (*Zeit. physikal. Chem.*, 1890, **6**, 450).

It will be noticed that the ratio of the mean molecular weight observed (by boiling point method) to the true molecular weight is $365/443 = 0·824$ for lead tetracetate, and $69/82 = 0·841$ for sodium acetate.

Molecular Volume of Lead Tetracetate.—The formula $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ obtained some slight additional support from the fact that, taking the specific gravity as 2·228, we find that the molecular volume is 199, a number which agrees well with that calculated by the aid of the empirical law enunciated by Schröder (*Ber.*, 1881, **14**, 1607), namely, that for a large number of anhydrous acetates the molecular volume of the salt is the same as that of the molecules of acetic acid from which it has been derived. This statement is illustrated in the following table.

Salt.	MV.	Salt.	MV.	Salt.	MV.
$C_2H_4O_2$	48·7	$2C_2H_4O_2$	97·5	$4C_2H_4O_2$	195
$C_2H_3O_2 \cdot Na$	53·8	$(C_2H_3O_2)_2Mg$..	99·9	$(C_2H_3O_2)_4Pb$...	199
$C_2H_3O_2Ag$	51·5	„ Zn ..	99·5		
		„ Ni ..	98·5		
		„ Mn ..	99·1		
		„ Sr ..	97·9		
		„ Hg ..	97·2		
		„ Pb ..	99·9		

Action of Water.—Lead tetracetate is extraordinarily sensitive to the presence of water, so much so, indeed, that exposure to the air for a few moments suffices to turn it brown. The interaction represented by the equation $Pb(C_2H_3O_2)_4 + 2H_2O = PbO_2 + 4C_2H_4O_2$, takes place quantitatively, and forms the basis of the method of analysing the salt used by Jacquelain and ourselves. This salt might sometimes be useful for detecting the presence of moisture in gases.

Action of Hydrochloric acid.—Lead tetracetate is readily dissolved by concentrated aqueous hydrochloric acid, giving a deep yellow solution, which contains lead tetrachloride, produced in accordance with the equation $Pb(C_2H_3O_2)_4 + 4HCl = PbCl_4 + 4C_2H_4O_2$. The lead tetrachloride cannot, however, be directly isolated, and, on standing, or more quickly on warming, the yellow colour disappears, chlorine is given off and lead dichloride is left, whilst, in all probability, partial chlorination of the acetic acid occurs at the same time.

The existence of lead tetrachloride in this liquid may, nevertheless, be readily demonstrated by pouring it into dilute aqueous hydrochloric acid, saturated with ammonium chloride, when the double salt, $PbCl_4 \cdot 2NH_4Cl$, at once separates as a yellow precipitate. A salt of this nature was isolated in 1885 by Nikolukine (*Abstr.*, 1886, 123; from *J. Russ. Chem. Soc.*, 1885, 207) from the solution of lead dioxide in hydrochloric acid, but he does not appear to have assigned any formula to it. Some years later, Classen and Zahorski (*Zeit. anorg. Chem.*, 1893, 4, 100) prepared the salt $2PbCl_4 \cdot 5NH_4Cl$, by adding concentrated ammonium chloride solution to the homogeneous liquid obtained when lead dichloride, concentrated hydrochloric acid, and liquid chlorine were digested together for some hours.

Substituting quinoline hydrochloride for ammonium chloride, they obtained from the same solution the salt $PbCl_4 \cdot 2C_9NH_7HCl$.

Wells (*Zeit. anorg. Chem.*, 1893, 4, 335), on the other hand, and Friedrich (*Ber.*, 1893, 26, 1434) are both of opinion that the formula

of the ammonium salt is really $\text{PbCl}_4, 2\text{NH}_4\text{Cl}$. The former obtained it by adding ammonium chloride dissolved in hydrochloric acid to a solution of lead dioxide in the same acid, and made the corresponding potassium, rubidium, and caesium compounds by a similar process. The latter worked with a solution of lead tetrachloride prepared by passing chlorine gas into lead dichloride dissolved in aqueous hydrochloric acid.

Goebbels (*Ber.*, 1895, **28**, 792) has recently sought to explain this discrepancy by assuming that two sets of double salts exist, of the types $\text{PbCl}_4, 2\text{M}'\text{Cl}$ and $2\text{PbCl}_4, 5\text{M}'\text{Cl}$ respectively, and claims to have prepared the two corresponding lutidine compounds, and also a picoline salt, $3\text{PbCl}_4, 7\text{C}_6\text{NH}_7, \text{HCl}$, belonging to a different type.

Finding that ammonium chloride was precipitated from its saturated aqueous solution on the addition of hydrochloric acid, we endeavoured, when preparing our salt, to avoid this source of impurity by using, as Wells had done, a solution of ammonium chloride in hydrochloric acid.

The following analyses show that the salt obtained by us under these conditions is identical with those prepared by Wells and Friedrich.

- I. 0.6888 gave 0.4590 PbSO_4 . $\text{Pb} = 45.51$.
 - II. 0.5437 „ 1.0234 AgCl . $\text{Cl} = 46.54$.
 - III. 0.7905 required 35.1 c.c. of $\text{Na}_2\text{S}_2\text{O}_3$. Cl (active) = 15.21.
(1 c.c. = 0.2396 $\text{Na}_2\text{S}_2\text{O}_3$).
- $\text{PbCl}_4, 2\text{NH}_4\text{Cl}$ requires $\text{Pb} = 45.39$, $\text{Cl} = 46.71$, Cl (active) = 15.57 per cent.

Action of Gaseous Hydrogen Chloride.—This gas, dried by means of sulphuric acid, acts energetically on lead tetracetate in accordance with the equation given above, and in the early part of 1893, we made numerous attempts to separate the acetic acid from the tetrachloride by means of carbon tetrachloride and other liquids. Our efforts in this direction met with no success until we learnt from Friedrich's paper (*Ber.*, 1893, **26**, 1434) that lead tetrachloride is not acted on by sulphuric acid, when by employing this acid we were able to prepare small quantities of lead tetrachloride direct from the tetracetate. For this purpose, a few grams of the finely powdered salt were placed in a test tube and covered with concentrated sulphuric acid.

The tube was then quickly cooled in ice, and dry hydrogen chloride was passed in; after a short time, a globule of lead tetrachloride collected at the bottom of the tube. The yield was unfortunately small, the greater portion of the lead being converted into sulphate. A similar result, but a still poorer yield, was obtained

by passing hydrogen chloride over lead tetracetate kept cool in ice; on adding cold, concentrated sulphuric acid, the acetic acid was dissolved, and a small globule of lead tetrachloride remained.

Action of Hydrobromic and Hydriodic acids.—Lead tetracetate dissolves in the concentrated acids, but almost immediate separation of the halogen and corresponding haloïd occurs. We have not succeeded in isolating double salts from the solutions, but Classen and Zahorski have prepared the two quinoline derivatives, $\text{PbBr}_4 \cdot 2\text{C}_9\text{NH}_7 \cdot \text{HBr}$ and $\text{PbI}_4 \cdot 2\text{C}_9\text{NH}_7 \cdot \text{HI}$, by decomposing the chloride with potassium bromide and iodide respectively.

Action of Hydrofluoric acid.—The aqueous acid (37 per cent.) dissolves lead tetracetate readily, and gives a colourless solution, which, in all probability, contains either PbF_4 or H_2PbF_6 . If excess of acid is present, the solution is stable at the ordinary temperature, but, like the liquid obtained when hydrochloric acid is used, it is entirely broken up on evaporation even in a vacuum; the decomposition in this case, however, takes a somewhat different course, and results in the quantitative deposition of lead dioxide in accordance with the equation $\text{PbF}_4 + 2\text{H}_2\text{O} = \text{PbO}_2 + 4\text{HF}$.

The explanation of this difference in the behaviour of the two haloïds is most likely to be sought in the small relative affinity of hydrofluoric acid as compared with hydrochloric acid.

The hydrofluoric acid solution of the tetracetate may, however, be evaporated to dryness without separation of lead dioxide if a small quantity of ammonium fluoride is first added to it, and leaves then a residue rich in quadrivalent lead. This is, doubtless, due to the formation of an ammonium double salt analogous to those derived from lead tetrachloride.*

Action of Hydrogen Sulphide.—In view of the ease with which water and lead tetracetate interact to form lead dioxide, we thought it desirable to see if a corresponding sulphide, PbS_2 , could be prepared by passing hydrogen sulphide over the salt or into its solutions in glacial acetic acid or chloroform. The product, in all cases, appeared to consist of lead sulphide and free sulphur, and we have been quite unable to obtain any evidence of the existence of the bisulphide PbS_2 .

* We obtained the above results in the summer of 1893, but were unable to continue the research till the following spring. In the meantime, several points we had proposed to investigate, were cleared up in an interesting paper by Brauner (*Trans.*, 1894, 65, 393), who, unknown to us, had been working on the same lines as ourselves, and who by a similar method to the above, succeeded in preparing considerable quantities of the salt $\text{PbF}_4 \cdot 3\text{KF} \cdot \text{HF}$, isomorphous with the corresponding tin compound, pink salt, $\text{SnF}_4 \cdot 3\text{KF} \cdot \text{HF}$, and pointed out that after hydrofluoric acid had been expelled by heating at 250° , the residue yielded fluorine on ignition.

Action of Sulphuric acid.—Lead tetracetate is insoluble in aqueous sulphuric acid, which rapidly converts it into lead dioxide. When treated with the concentrated acid at ordinary temperatures, no change occurs at first, but after a time the salt turns yellow, slowly gelatinises, and finally decomposes, lead sulphate being deposited, and a small quantity of gas chiefly consisting of carbon dioxide evolved. This change takes place at once if the acid and salt are warmed together on the water bath; under these conditions, lead tetrasulphate, $\text{Pb}(\text{SO}_4)_2$, if formed, is exceedingly unstable, and we have not been able to obtain any satisfactory proof of its existence. Brauner (*Zeit. anorg. Chem.*, 1894, **7**, 11), however, found that a clear solution of lead tetrafluoride in excess of concentrated sulphuric acid deposited yellow crusts, believed by him to be $\text{Pb}(\text{SO}_4)_2$ when it was warmed to 100° from time to time, during a period of more than two months.

Lead Tetraphosphate.

When a 50 per cent. aqueous solution of orthophosphoric acid is allowed to act on lead tetracetate, the latter is converted into a pale yellow gelatinous mass, which readily turns brown on adding excess of water, and evolves chlorine when treated with hydrochloric acid. These observations led us to make numerous attempts to prepare phosphates of quadrivalent lead, and though we have not so far been successful in preparing a pure specimen of such a compound, we believe, nevertheless, that our results warrant the assertion that $\text{Pb}(\text{HPO}_4)_2$ is capable of existence, and we attribute our inability to obtain it pure chiefly to the lack of a suitable solvent for lead tetracetate, and also to the difficulty of washing away excess of phosphoric acid, without at the same time decomposing the tetraphosphate formed. In the course of this part of our work, a large number of preparations has been made and analysed; we only propose, however, to describe a few experiments which either illustrate our methods or give information as to the nature of the compounds obtained.

1. Lead tetracetate was dissolved in glacial acetic acid, excess of aqueous phosphoric acid added, and the white gelatinous precipitate, after being collected on a filter plate, and washed first with acetic acid and finally with absolute alcohol, was then placed over sulphuric acid in a vacuum till all smell of acetic acid had disappeared. The solid obtained turned brown when treated with water, and contained 7.9 per cent. of quadrivalent lead, Pb^{IV} (determined by distillation with hydrochloric acid) 52 per cent. of bivalent lead, Pb^{II} (total lead — Pb^{IV}) and 12.54 per cent. of phosphorus. $\text{Pb} : \text{P} = 1 : 1.417$. Two orthophosphates of lead $\text{Pb}_3(\text{PO}_4)_2$ and PbHPO_4 have been described. They contain Pb and P in the ratio 1 : 0.666 and 1 : 1 respectively.

Corresponding phosphates of quadrivalent lead would be $\text{Pb}_3(\text{PO}_4)_4$ and $\text{Pb}(\text{HPO}_4)_2$, with the ratio $\text{Pb} : \text{P} = 1 : 1.333$ and $1 : 2$. The analysis shows that the sample contains more phosphorus than would be found if all the bivalent lead were present as PbHPO_4 , and the quadrivalent lead as $\text{Pb}(\text{HPO}_4)_2$; this is doubtless due to imperfect washing, while the explanation of the small amount of quadrivalent lead is to be sought in the reducing action of the absolute alcohol.

2. It was subsequently found that much better results could be obtained by adding a solution of tetracetate in acetic acid to a concentrated solution of aqueous phosphoric acid, mixed with two or three times its volume of acetic acid. The precipitate which formed was sucked up, washed quickly with acetic acid only, and dried as completely as possible in a vacuum over sulphuric acid and solid caustic soda. This specimen proved, on analysis, to be entirely free from bivalent lead, whilst quadrivalent lead and phosphorus were present in the ratio $1 : 2.36$. Owing to the presence of excess of phosphoric acid as an impurity we have not been able to assign a definite formula to this compound, the fact that all the lead is quadrivalent proves, however, quite conclusively that tetraphosphates of lead can be prepared by precipitation.

3. Lead tetracetate is only slightly soluble in cold glacial acetic acid, and any method involving the use of large quantities of such a solvent is open to so many objections that we resolved to try and precipitate chloroform solutions of the tetracetate by alcoholic phosphoric acid. Preliminary experiments showed us that the salts obtained in this way contained considerable quantities of quadrivalent lead, and were fairly stable in the presence of alcoholic phosphoric acid.

a. Five grams of lead tetracetate were moistened with acetic acid, dissolved in 75 grams of chloroform, and the solution poured slowly into 14.75 grams of a 30 per cent. alcoholic solution of H_3PO_4 (4 mols. $\text{H}_3\text{PO}_4 : 1$ mol. PbAc_4), the precipitate at first redissolved, but became permanent after the greater part of the solution of lead tetracetate had been added. On adding ether, a bulky solid came down, which filtered readily, and was soluble in water, giving a brown liquid from which lead dioxide was precipitated on boiling. Alcohol acted on the precipitate, dissolving some of it, and converting the rest into a yellow, semi-transparent jelly, which it was almost impossible to filter. After sucking it up as completely as possible with the aid of a pump, it was placed in a vacuum till it dried to a white mass.

The lead in this substance was probably all quadrivalent, for although, owing to the presence of alcohol in the apparently dry mass, no satisfactory determination could be made, still, in spite of the reducing action of the alcohol, upwards of 80 per cent. of the total

lead was found to be present as Pb^{IV} . After heating for some time at 150° , a portion of the substance was gently ignited; the residue contained Pb, 50.45; P, 19.68 per cent. $\text{Pb} : \text{P} = 1 : 2.605$.

b. Another specimen, prepared in a similar way, gave a salt which, after drying at 150° , was found to contain Pb, 52.9; P, 15.63 per cent. It lost, on ignition, 5.07 per cent., and the composition of the residue, calculated from these data, is Pb, 56.2 and P, 16.61 per cent. $\text{Pb} : \text{P} = 1 : 1.99$ (mean of three analyses). From these numbers it will be seen that in this sample the ratio $\text{Pb} : \text{P}$ is that required by the formula $\text{Pb}(\text{HPO}_4)_2$. This may be a mere coincidence, but it seems to us highly probable that this substance was actually formed, for its composition, Pb, 51.88 and P, 15.54 per cent., agrees fairly well with that of our preparation. Again, if we grant that such a substance as $\text{Pb}(\text{HPO}_4)_2$ may exist, we may fairly be allowed to assume that it will give off water and oxygen on ignition, and be converted into the metaphosphate ($\text{Pb}(\text{PO}_3)_2$). This change will result in a loss of 7.39 per cent., and the residue will contain Pb, 56.71 and P, 16.98 per cent. The numbers quoted above as representing the actual composition of the ignited substance agree fairly well with these. It is probable that our preparation while drying at 150° underwent a certain amount of decomposition, and this would account for its containing rather more lead and phosphorus than the formula $\text{Pb}(\text{HPO}_4)_2$ demands, and also to some extent for the small loss when it was subsequently ignited.

It is, perhaps, worth noticing in this connection that the composition of the residue obtained in Experiment 3a may be also fairly satisfactorily explained if we assume that the substance before ignition consisted of a mixture of $\text{Pb}(\text{HPO}_4)_2$ and H_3PO_4 , and that these on heating were converted into $\text{Pb}(\text{PO}_3)_2$ and HPO_3 respectively, for if we calculate and subtract the weight of HPO_3 , which corresponds to the excess of phosphorus present, the residue has the composition $\text{Pb} = 57.21$ and $\text{P} = 17.17$ per cent., while $\text{Pb}(\text{PO}_3)_2$ requires Pb, 56.71 and P, 16.98 per cent.

If all the lead in these two compounds had been present in the quadrivalent state, a strong case would have been made out for assigning the formula $\text{Pb}(\text{HPO}_4)_2$ to our precipitate.

Determinations made by distillations with hydrochloric acid showed, however, that of the total lead in 3a, only 80 per cent., and in 3b, only 65 per cent. was present as quadrivalent lead. We are, however, inclined to think that this result was due, partly to reduction of the tetrphosphate during its preparation, and possibly also to the presence of small quantities of alcohol in the apparently dry substance, which, being acted on by the chlorine evolved, vitiated the determination. We believe, however, that the facts we have quoted,

though insufficient to establish the formula $\text{Pb}(\text{HPO}_4)_2$, make it extremely probable that this compound was actually precipitated.

This point cannot, however, be satisfactorily settled without further experimental work, and we hope to find an early opportunity of submitting this substance to a more thorough examination.*

Lead Tetrapropionate.

This salt resembles the corresponding acetate very closely, and was prepared and analysed in a precisely similar way. It crystallises from its solution in propionic acid in thin needles, which melt at 132° , and decompose at a somewhat higher temperature. The substance can be recrystallised from hot propionic acid, but the process is attended with loss, a portion of the tetrapropionate being apparently reduced to propionate.

The sample analysed was recrystallised twice.

0.6389 gave 0.3077 PbO_2 , and required 51.7 c.c. of soda solution [1 c.c. = 0.00395 gram NaOH], whence $\text{PbO}_2 = 48.16$ and $(\text{C}_3\text{H}_5\text{O})_2\text{O} = 51.94$ per cent.

0.3870 gave 0.2172 PbCl_2 , whence $\text{PbO}_2 = 48.26$ per cent. The formula $\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_4$ requires $\text{PbO}_2 = 47.87$ and $(\text{C}_3\text{H}_5\text{O})_2\text{O} = 52.13$ per cent.

Analogous Salts of other Metals.

The existence of a stable crystalline acetate derived from lead dioxide led us to enquire if the higher oxides of other metals afford similar compounds. We find that several such substances have been described, the most interesting of which are the thallic and manganic acetates. According to Willm (*Ann. Chim. Phys.*, 1865, [4], 5, 5), the acetate, $\text{Tl}(\text{C}_2\text{H}_3\text{O}_2)_3$, obtained by dissolving freshly precipitated thallic oxide in strong acetic acid, is the most stable of the thallic salts. Like lead tetracetate, which it resembles extraordinarily closely, it is quantitatively decomposed, on treatment with water, into Tl_2O_3 and acetic acid. It is soluble in hydrochloric acid, giving thallic chloride; added to potassium iodide it sets free iodine, thallous iodide being precipitated, whilst phosphoric and arsenic acids give gelatinous precipitates, probably consisting of $\text{TlPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{TlAsO}_4 \cdot 2\text{H}_2\text{O}$ respectively. Thallic chloride and the thallic salts generally are,

* By methods somewhat similar to those employed for preparing the lead tetraphosphate described above, we have recently succeeded in obtaining a lead tetraarsenate, containing 42.01 per cent. of lead, and 30.59 per cent. of arsenic; the formula $\text{Pb}(\text{HAsO}_4)_2$ requires Pb, 42.48 per cent., and As, 30.83 per cent. This substance, together with some others made by acting with a hydrofluoric acid solution of lead tetracetate on solutions of phosphoric acid, are still under investigation, and we hope soon to make a further communication to the Society on this subject.

however, somewhat more stable than the plumbic salts, and the nitrate, sulphate, and oxalate have been prepared.

Like lead dioxide, manganic oxide, Mn_2O_3 , is not attacked by acetic acid, the oxide Mn_3O_4 , however, dissolves readily enough, and on adding a little water, crystals of $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 2\text{H}_2\text{O}$ are deposited (Christensen, *J. pr. Chem.*, 1883, [2], 28, 1). This salt is apparently the most stable of the manganic compounds, and its behaviour towards reagents is similar to that of lead tetracetate; a sulphate, $\text{Mn}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$; phosphates, $\text{MnPO}_4 \cdot \text{H}_2\text{O}$, and $\text{MnNaP}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$, and an arsenate, $\text{MnAsO}_4 \cdot \text{H}_2\text{O}$, have been prepared from it. Christensen has also described a fluoride, $\text{MnF}_3 \cdot 3\text{H}_2\text{O}$, and numerous double salts of the type $2\text{M}'\text{F}, \text{MnF}_3$ (*J. pr. Chem.*, 1887, [2], 35, 57).

Cobaltic acetate exists in the solution prepared by dissolving hydrated cobaltic oxide in strong acetic acid (Beetz, *Ann. Phys. Chem.*, 1844, 61, 472). With the exception of the sulphate described by Marshall (*Trans.*, 1891, 59, 767), it seems to be the most stable of the simple cobaltic salts. When the oxide, CrO_3 , dissolves in glacial acetic acid, an acetate may possibly be found; we have not, however, been able as yet to obtain any evidence of this.*

List of Salts of Quadrivalent Lead.

Leaving out of consideration the numerous organo-metallic derivatives of lead, and omitting a few compounds whose nature is not yet fully elucidated (Wells, *Zeit. anorg. Chem.*, 1895, 9, 305), the following list comprises the salts of quadrivalent lead which have, up to the present, been described by Brauner, Classen and Zahorski, Friedrich, Goebbel, Wells, and ourselves.

$\text{PbF}_4?$	PbCl_4 .
$\text{PbF}_4, 3\text{KF}, \text{HF}$.	K_2PbCl_6 .
	Rb_2PbCl_6 .
	Cs_2PbCl_6 .
	$(\text{NH}_4)_2\text{PbCl}_6$.
	$(\text{C}_9\text{NH}_7)_2, \text{H}_2\text{PbCl}_6$, $(\text{C}_9\text{NH}_7)_2, \text{H}_2\text{PbBr}_6$, and
	$(\text{C}_9\text{NH}_7)_2, \text{H}_2\text{PbI}_6$.
	$(\text{C}_7\text{NH}_9)_2, \text{H}_2\text{PbCl}_6$.
	$2\text{PbCl}_4, 5\text{NH}_4\text{Cl}$.
	$2\text{PbCl}_4, 5(\text{C}_5\text{NH}_5, \text{HCl})$ (pyridine salt).
	$2\text{PbCl}_4, 5(\text{C}_7\text{NH}_9, \text{HCl})$ (lutidine salt).
	$3\text{PbCl}_4, 7(\text{C}_6\text{NH}_7, \text{HCl})$ (picoline salt).
$\text{Pb}(\text{SO}_4)_2?$	$\text{Pb}(\text{HPO}_4)_2?$
	$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$
	$\text{Pb}(\text{C}_3\text{H}_5\text{O}_2)_4$.
	$\text{Pb}(\text{HAsO}_4)_2$.

* The remarkable compound obtained by Tafel (*Ber.*, 1894, 27, 816) by acting with Na_2O_2 on acetic acid, does not appear to belong to this class of substances.

Brauner, Friedrich, and Wells have pointed out that several of these compounds present analogies not only in composition, but also in behaviour and crystalline form, with certain of the stannic salts, and the relationship between lead and tin is further exhibited by the existence of plumbates allied to the stannates. Of them the potassium, sodium, barium, strontium, and calcium salts have been prepared, whilst the two oxides Pb_2O_3 and Pb_3O_4 , may be regarded as derivatives of meta- and ortho-plumbic acids respectively, and may therefore be written PbO, PbO_2 and $\left. \begin{smallmatrix} \text{PbO} \\ \text{PbO} \end{smallmatrix} \right\} \text{PbO}_2$.

In conclusion, the principal results of our work, and our deductions from them, may be summed up as follows.

1. The substance obtained by dissolved Pb_3O_4 in glacial acetic acid has the molecular formula $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$. It is decomposed quantitatively by water into lead dioxide and acetic acid; hydrochloric acid converts it into lead tetrachloride, and orthophosphoric acid into a phosphate. Its general behaviour is analogous to that of the thallic and manganic acetates, and its molecular volume agrees with that calculated for the acetates by Schröder's empirical law.

These facts lead us to regard it as a salt of lead dioxide.

2. A similar propionate exists.

3. When acted on by orthophosphoric acid, the tetracetate is converted into a phosphate, to which in all probability the formula $\text{Pb}(\text{HPO}_4)_2$ must be assigned.

4. Numerous lead salts exist which bear the same relation to the stannic salts that the ordinary lead compounds do to the stannous salts. The former should therefore be termed plumbic salts, and the latter plumbous salts.

5. Like stannic oxide, lead dioxide is capable of playing the part of either an acid or a basic oxide. The appropriate name for it is plumbic oxide, which should be used in preference to the term peroxide, which in this connection is both unsuitable and misleading.

*Mineralogical Museum,
Cambridge.*

XXIV.—*The Acetylene Theory of Luminosity.*

By VIVIAN B. LEWES, Royal Naval College, Greenwich.

EARLY in 1892 (Trans., 1892, **61**, 322), I read a paper before the Chemical Society, in which I showed that in a luminous hydrocarbon flame the baking effect of the outer zone of intense combustion converted a very large proportion of the unsaturated hydrocarbons

present in the inner zone into acetylene, the maximum production of this compound taking place just before the commencement of luminosity.

In a second paper, communicated to the Royal Society in 1895 (*Proc. Roy. Soc.*, 57, 450), I gave experimental reasons for considering that the acetylene so formed on its decomposition by heat into carbon and hydrogen was the main factor in producing luminosity, as the heat developed by this decomposition raised the carbon particles to a temperature above that of the flame.

At the time that the latter paper was published, I was unaware that any other work had been done in this direction, but I find that Professors Dewar and Liveing, in their beautiful work on the spectra of carbon and its compounds, had to a great extent forestalled the conclusions to which I had arrived from a totally different standpoint.

In their paper "On the Origin of the Hydrocarbon Flame Spectrum" (*Proc. Roy. Soc.*, 1882, 34, 427), they say, when speaking of the flame of cyanogen and acetylene, "Both of these compounds decompose with evolution of heat, in fact they are explosive compounds, and the latent energy in the respective bodies is so great that, if kinetic in the separated constituents, it would raise the temperature between 3000° and 4000° . The flames of cyanogen and acetylene are peculiar in respect that the temperature of individual decomposing molecules is not dependent entirely on the temperature generated by the combustion, which is a function of the tension of dissociation of the oxidised products, carbonic acid and water. We have no means of defining with any accuracy the temperature which the particles of such a flame may reach. We know, however, that the mean temperature of the flames of carbonic oxide and hydrogen lies between 2000° and 3000° , and if to this be added that which can be reached independently by the mere decomposition of cyanogen or acetylene, then we may safely infer that the temperature of individual molecules of carbon, nitrogen, and hydrogen in the respective flames of cyanogen and acetylene, may reach a temperature of from 6000° to 7000° ."

"A previous estimate of the temperature of the positive pole in the electric arc made by one of us gave something like the same value.

* * * * *

"The formation of acetylene in ordinary combustion seems to be the agent through which a very high local temperature is produced"

I extremely regret not having known of this most valuable work before, and take this, the first opportunity afforded me, of drawing attention to it.

I also find that M. Guéguen (*Compte rendu du Société Technique de l'Industrie du Gaz au France*, 1884, 142) pointed out that it was very probable that luminosity in hydrocarbon flames is due exclusively to the production of rays furnished by the molecules of gas highly heated by chemical changes, and that it must be borne in mind that the heating from exterior sources would not suffice whatever its power. He also draws attention to the fact that luminous combustion is caused by bodies which are endothermic, and from which heat is liberated during decomposition.

In November, 1895, Professor Smithells read a paper before the Chemical Society in which he criticises some of the less important points brought forward by me in my previous papers, and without attempting to disprove the fact that acetylene undergoes luminous decomposition when heated apart from air or oxygen, the principal fact upon which the acetylene theory of the luminosity of hydrocarbon flames is based, comes to the final conclusion that if the criticism he offers is just "then the acetylene theory of luminosity will share the fate of the 'dense hydrocarbon' theory."

The first portion of his paper is devoted to the measurement of flame temperature by means of the Le Chatelier thermo-couple, and he comes to the conclusion that the experiments show two things. 1. The fallacious results that may be obtained by not disposing the couple with due regard to the conformation of the zone of flame to be measured. 2. The difficulty of ascertaining the increase of temperature contributed by the chemical changes occurring in any one spot.

The first conclusion is self-evident, and the second I have already warmly endorsed in the paper which Professor Smithells is criticising (*Proc. Roy. Soc.*, 1895, 57, 452).

He then proceeds to explore the temperatures existing in a luminous flat flame of coal gas, using for this purpose a No. 4 Bray's union jet burner at a gas pressure of $2\frac{1}{2}$ in. of water. As Professor Smithells considers the temperature determinations which he made as practically valueless, it is not necessary to criticise the pressure used, which should have been $7/10$ ths rather than $2\frac{1}{2}$ in. Considering, however, the abnormal character of the flame with which he was dealing, his figures accord fairly well with those I have given as representing the gradual rise of temperature in the inner zone of a luminous flat flame, and this is of interest, as the methods employed were slightly different, and the coincidence of result goes some way towards establishing the probability of the figures.

In considering the temperature in the flat flame, Professor Smithells says: "To obtain any useful measurements for this flame it is obvious that it can be explored in one way only, namely, by lay-

ing the junction and the adjacent wires in a horizontal straight line, and introducing it along the flat face of the flame so that it may be placed with a considerable length of wires immersed symmetrically in any one sheath and passing through parts of the flame in like condition." Having then taken the temperature of the outer and inner zones in this way, he proceeds to say: "The measurements for the inner parts of the flame above given have only a negative significance. It is obvious that they cannot be true temperatures as the wires have always to be thrust through the hot outer sheath of flame, and, moreover, the couple would attain by radiation from the outer walls a higher temperature than the rapid stream of gas in which it is immersed."

With regard to the first objection, that the wires have to pass through the outer wall of high temperature, and that this will invalidate the reading, I think he is mistaken; there will be nearly an inch of heated wire between the thermo-couple and the point where the wires pass through the outer zone, and it seems to me that any conduction from these bodies will be more likely to take place outward along the cool wire than inwards to the heated zone, so that if an equal length of wire on each side of the weld is heated in order to prevent unequal resistances being introduced, the readings should not suffer much from this cause.

Nor does his second objection appear to me to be in any way a fatal one. If the gases in the inner zone had to pass through a circle or even a belt of high temperature, the objection would be valid, but, inasmuch as the gases are flowing up within a sheath of high temperature which exists even after the inner zone ceases to exist, and which is fairly constant in temperature, these gases will probably be as much exposed to radiation as the thermo-couple.

In taking such readings the thermo-couple is only exposed in the heated zone for a very short period, and it has been pointed out by Le Chatelier that the couple takes up the temperature of the locality in which it is placed with astonishing rapidity, whilst Mr. Callendar has pointed out (*Trans. Roy. Soc.*, 1892, 166) that a spiral of platinum wire is a bad radiator, and is exceedingly sensitive to slight changes in temperature; it may be assumed, therefore, that it will not absorb radiant heat with great rapidity, and that the temperatures recorded in the non-luminous zone are not far removed from the truth.

Professor Smithells further accentuates his distrust of these recorded temperatures by saying "the readings are not even comparable, as the flame varies in breadth and thickness from point to point in a vertical plane."

The inner zone undoubtedly becomes narrower in the higher

regions of the flame until ultimately the outer walls meet at the top of the flame, but the rise of temperature due to this cause is one of the factors that aid the generation of light in a flame, and if a gas were flowing up a gradually narrowing tube heated throughout to an even temperature, it would manifestly become hotter the nearer the walls of the tube approached each other, and I cannot understand why, because the thermo-couple records this fact, the readings are to be discredited.

In the determinations which I made of the temperatures existing in the flame from a No. 6 Bray's union jet burner, I did not attempt to take the temperature of the outer zone, as it was manifest that this would be the hottest part of the flame, and I felt that it would be hopeless to get any accurate readings of it, as it seems clear that close to the inner zone, where there is the maximum of combustible gas meeting with oxygen for its combustion, there will be the hottest part of the flame, whilst the admixture of nitrogen, air, and the escaping products of combustion will cause a rapid fall in temperature to the outer portion of this zone, which extends much farther than mere observation of the flame would lead one to expect, and that in the outer envelope there are so many gradations of temperature from the hottest to the coolest portion where combustion is finally extinguished, that it would be impossible to obtain even a general idea of its temperature, and the main point which I wished to ascertain was the effect this high temperature layer of combustion had on the gases flowing up through the inner zone.

The question of passing the wires of the thermo-couple through this heated layer before the inner zone could be reached of course presented itself at the commencement of the experiments, and, after trying several methods, including the one adopted by Professor Smithells, I came to the conclusion that the best way of doing it was to make the twist of the thermo-couple very short, and to bend each wire at right angles three-quarters of an inch on each side of the couple, so that on plunging it into the flame an equal length of wire on each side of the twist was equally heated, whilst the portions of the wire passing through the more highly heated zones were equidistant from the couple, thus ensuring no unequal resistances being introduced.

In my later experiments, I have employed a fixed stand for burner and thermo-couple, so that the exact position of the couple could be accurately determined, and in this case the wires come out at the side of the flame, as in Professor Smithells' experiments, but the thermo-couple being fixed immediately over the centre of the burner, an equal length of wire is heated on each side of the couple.

The use of the Le Chatelier thermo-couple for the determination of

high temperatures is now becoming so general that a description of the precautions necessary in using it will not be out of place, and in my later experiments these were employed.

The thermo-couple was connected in series with a dead-beat galvanometer—Ayrton and Matthers' pattern—having a resistance of 304 ohms, and in order to bring the deflections for the high temperatures within the limits of the scale, a further resistance of 309 ohms was included in the circuit.

The galvanometer was calibrated by means of a cell of small internal resistance and a box of high resistance coils, and, on plotting out the currents and deflections, a straight line was obtained, showing that within the limits of the scale the deflections were directly proportional to the currents.

The platinum and platinum-rhodium wires used for the thermo-couple were 0.011 inch in diameter, or 0.279 mm., which is the thinnest that can be used without fear of fusion at the highest temperature of the flame. The resistance of the platinum wire per metre was 1.71 ohms, that of the platinum-rhodium wire being 3.6 ohms.

In the experiments described by Professor Smithells, the total resistance of wire and galvanometer was about 4 ohms, which enormously increases the risk of error.

The galvanometer and lamp being fixed on a stand, so as to give no possibility of displacement, the couple and galvanometer were calibrated for temperature, the fixed points selected being the following.

Boiling point of sulphur.....	444.5° C.
Melting point of pure silver.....	945.0 „
„ „ copper.....	1045.0 „
„ „ palladium	1500.0 „
„ „ platinum	1775.0 „

The melting points of the compounds of the alkalis and alkaline earths vary so widely, as determined by different observers, that they are practically useless for this purpose, and, as there seemed to be some doubt as to whether the E.M.F. of the thermo-couple is directly proportional to temperatures above 1000°, I made 13 determinations of the fusing point of palladium and 16 of platinum, and, on plotting out a curve for the temperatures, obtained a straight line for all except the palladium, which was above the line. L. Holborn and W. Wein (*Ann. Phys. Chem.*, 1895, **56**, 360) find the melting point of palladium to be 1587°, and, had this figure been taken, it would have been close to the same line as the others.

From this, I think it is safe to assume that the course of the curve continues in a straight line above 1000°.

In continuing his paper, Professor Smithells proceeds to criticise

the values which he obtained for the outer envelope of the flame, and by testing this portion with a thin platinum wire, which he heats to fusion, comes to the conclusion that his results give a temperature slope opposite to that given by the thermo-couple, *i.e.*, that the hottest portion of the outer envelope of the flame is near the bottom, and explains this as being caused by variations in the thickness of the outer sheath of combustion.

In supposing that this is so, I think Professor Smithells is right as to his facts but wrong as to the causes to which he ascribes them, as the combustion which gives the outer envelope to the flame in the lower half is mainly due to marsh gas and hydrogen diffusing out from the gas itself, whilst, in the upper portion of the flame, it is due to carbon monoxide and hydrogen produced by the actions in the flame, the combustible gases being diluted by the products of the actions taking place, and one would expect, therefore, that the lower portion of the non-luminous envelope would be hotter than the upper, although, in point of fact, the temperature differs but little, as the accumulation of heat from the combustion going on in the lower part of the flame tends to increase the temperature of the upper portion.

I am in entire accord with Professor Smithells' conclusion that there are two separate heat gradients in a luminous coal gas flame: one on the vertical axis, which is, in all probability, a steady decline from the top to the bottom; the second on a horizontal axis, showing, as we proceed from the centre of the unburnt gas, a steep ascent to the point of contact with the luminous sheath, then a still steeper ascent to the point of contact with the mantle, where the highest point is abruptly attained." That the temperature gradient on the vertical axis is a steady decline from top to bottom is perfectly clear from both our experiments, whilst that there is a second gradient in a horizontal axis, with the coolest point in the centre of the flame—which is at the greatest distance from the source of heat—is, I think, a foregone conclusion, and I cannot conceive any other condition.

The second conclusion is that the temperature of the mantle of a coal-gas flame is above the melting point of platinum, and cannot, therefore, be determined by a thermo-couple in which platinum is one of the elements. Professor Smithells' own experiments show his thermo-couple registered a temperature there of 1478° at the bottom of the sheath to 1613° at the top of the flame, and his assumption, therefore, that the temperature exceeds that necessary for melting platinum is dependent on the melting in the outer mantle of very fine platinum wire.

In my previous paper I have shown the influence which the thickness of the platinum and platinum-rhodium wire used has on the

temperature recorded, and have clearly pointed out that in all the experiments quoted in that paper, wires having a diameter of 0.011 inch or 0.279 mm., were employed.

Professor Smithells uses wires of nearly double this thickness, and obtains a recorded temperature of 1838° before his couple fuses, which, if corrected to the thickness of wire I employed, would be over 2000° . This is caused by the larger cross section of the wire, which is in the ratio of 3.2 to 1, which would lead to a proportionately larger amount of heat being lost by conduction. I found that during the determinations of the deflections corresponding to the fusion of platinum, great care had to be exercised in raising the temperature of the junction exactly to the melting point. It was, in all cases, the platinum of the junction which fused first, and, in some cases, the platinum-rhodium wire was surrounded by a film of melted platinum. It was easy, by carefully heating the junction with a small oxyhydrogen flame, to obtain readings far above the mean obtained for the melting point of platinum, showing that, although the platinum was in the liquid state, yet a thermo-current was obtained of greater strength than at the temperature of the simple fusion of platinum.

Professor Smithells makes a strong point of the fact that luminosity does not commence suddenly at a certain height, but appears as an envelope just below the inner surface of the outer zone, whilst the non-luminous zone continues inside the luminous zone to a considerable height in the flame. This manifestly must be so, as the decomposition of the diluted acetylene only takes place as particles stray close to the point where the highest temperatures exist, and as the centre of the inner zone is below the necessary temperature, the decomposition of this compound only takes place close to the point where the two zones coalesce. If flames of various illuminating powers are examined, it will be noticed that the greater the light emitted, that is, the richer the flame is in acetylene, the more marked is the commencement of luminosity, so that although the luminosity begins as a yellow haze with a poor coal-gas flame, it commences almost as a sharp line with a rich acetylene flame.

In concluding this portion of his paper, and in order to show the untrustworthy nature of the temperatures thus recorded, Professor Smithells takes two sets of the determinations of temperature existing in flat flames, made at periods of three years apart, the one with coal gas burning from a 0000 Bray, the other from a No. 6 Bray, and feels surprised that they do not show "parallelism." The temperatures given are

	0000 Bray.	No. 6 Bray.
Non-luminous zone.....	1023°	1014°
Commencement of luminosity..	1658	1267
Top luminous zone.....	2115	1368
Luminosity	practically nil.	about 13 candles.

When a flame of coal gas is spread out in an extremely fine sheet, as when burning from a 0000 Bray, the amount of air required for the complete combustion of the gas is much more quickly obtained, luminosity is considerably reduced, and a far higher temperature is attained, whilst the commencement of the feeble band of luminosity is also thrown far nearer the top of the flame, and must, therefore, be at a higher temperature. Had there been what Professor Smithells is pleased to call "parallelism," it would have given good grounds for suspecting the worthlessness of the determinations. Moreover, a thicker wire was used in the determinations taken with the No. 6 Bray in 1892, and I have fully pointed out the result of this.

An effective point is made by pointing out that one of these temperatures is 330° above the melting point of platinum, as determined by Violle. In any determination of the temperature of the luminous zone, the reading has to be taken with the greatest rapidity, as otherwise the formation of carbon on the couple causes a falling off in the temperature recorded. In the case instanced, the spot of light rapidly rose to the division which had been calibrated as 2116°, and then fell with great oscillations, and on removing the soot from the couple after cooling, it was found that the wires were welded together, and the platinum fused over the surface of the platinum-rhodium, the couple having evidently been only just saved from complete fusion by the deposition of the carbon.

The thermo-couple records with great rapidity the temperature attained by the outer surface of the metals, and it by no means follows that the moment needed to do this should be sufficient to raise the whole mass of metal to the melting point.

In my last paper, several temperatures of between 1800° and 1900° are recorded, and Professor Smithells fails to call attention to these, I presume, because he found in his own experiments, using wire of nearly double the thickness, that the couple recorded 1836° before fusion of the platinum in a hydrogen flame, whilst had he employed an oxyhydrogen flame, so as to very rapidly heat the couple, he would have found it easy to obtain still higher readings. I can only again repeat the statement made in my previous paper, that although flame temperatures taken by the Le Chatelier thermo-couple may be totally incorrect, they are, at any rate, comparable when proper precautions are taken in the methods of using the couple.

In the second part of his paper, Professor Smithells deals with other portions of my paper, and summarises his conclusions as follows.

1. The description of the structure of a flame adopted by Professor Lewes is not in harmony with the facts.

In the paper before referred to on "The Luminosity of Coal Gas Flames," *Chem. Soc.*, 1892, I gave the description of three zones of a luminous flame in the words to which Professor Smithells takes such strong exception.

In quoting this description, however, he entirely ignores the fact that the seven pages following are devoted to explaining the action of the air in rendering hydrocarbon flames non-luminous, this being done by tracing the action of diluents in destroying the luminosity of hydrocarbon gases in the Bunsen flame.

The results obtained make it perfectly clear that the outer zone of combustion must be the hottest part of the flame, but it is also manifest that between the layer of maximum temperature and the cool air there must be many gradations of temperature, and although I now realise that the outer zone of a flame extends further than I thought at that period, and that, therefore, the amount of products of incomplete combustion are extremely minute, I still believe that infinitesimal traces of carbon monoxide do escape combustion, and make themselves felt by delicate constitutions.

All my papers, also, clearly show that I consider it is the baking influence of the heat of combustion, generated in the outer zone of the flame, which leads to the changes taking place in the interior of the flame, and I fail to see why Professor Smithells should desire to make it appear that I look upon the outer zone of the flame as the coolest, instead of—as it undoubtedly is—the hottest part of the flame.

I should now be inclined to describe a coal-gas flame as consisting of two zones,

1. The outer envelope of combustion.
2. The inner region of non-combustion.

The outer zone is the portion of the flame where the combustible gases present in the original gas or generated by actions taking place in the inner zone meet with the air and undergo combustion, forming an envelope of intensely high temperature but no appreciable luminosity.

The maximum combustion takes place towards the inner side of the outer zone, as it is here that the largest proportion of the hot gases meet the oxygen of the air, the dilution and cooling effect produced by the air and products of combustion rapidly causing the

external portions of this zone to fall in temperature until finally extinguished.

The lower portion of the outer zone is chiefly due to hydrogen and methane which have diffused out from the coal gas undergoing combustion, whilst the upper portion of the outer zone is fed by carbon monoxide and hydrogen, formed by the decompositions and interactions taking place in the inner zone.

The inner zone is the region into which no oxygen penetrates, and in it many decompositions take place, due to the baking action of the heat generated in the outer zone, and to interaction with the products of combustion.

This zone may be sub-divided into three parts.

A. The non-luminous portion, in which the heavy hydrocarbons flowing upward from the burner rapidly increase in temperature owing to radiant heat from the outer flame walls, and are converted thereby into acetylene.

B. The luminous portion, which is produced by the acetylene formed in the flame, being heated to a temperature at which it is decomposed with such rapidity that the particles of carbon liberated are raised to incandescence by the heat generated by its own decomposition, the carbon particles being afterwards consumed by the carbon dioxide and water vapour diffusing into the flame from the outer zone, yielding carbon monoxide and hydrogen, which, together with the hydrogen liberated from the acetylene, give, by their combustion, the upper portion of the outer zone. This portion of the inner zone will only be formed near the point of maximum temperature, and therefore forms, in close contact with the outer zone, a sheath or cone which caps the non-luminous part.

C. The blue region at the base of the flame, which has, I believe, been generally ascribed to the hydrocarbons being consumed without liberation of carbon by the oxygen of the air. I am afraid I am here again at variance with the generally received ideas, as I believe this portion of the flame to be a continuation of the luminous portion in which the carbon dioxide and water vapour from the outer zone burn up the hydrocarbons to carbon monoxide and hydrogen before the temperature has risen sufficiently to decompose them into carbon and hydrogen.

If a luminous gas flame is turned down low, it is seen that as the luminosity disappears the blue region surrounds the inner zone, whilst it is in turn surrounded by the outer zone—an observation due, I believe, to Hildegard—and the small flame is rendered non-luminous, because there is not a sufficient body of heat to convert the hydrocarbons into acetylene, or if acetylene is formed, to decompose it before combustion. It is assumed, with a luminous flame, that no

oxygen penetrates through the outer zone, and as the outer zone still exists with the small flame, I fail to see why enough oxygen should enter to burn up the hydrocarbons before liberation of free carbon.

If a flame of acetylene be burnt at the end of an open tube, and carbon dioxide be allowed to gently flow up a second tube into the centre of the flame, the first addition destroys the smoky lurid nature of the flame, and gives a slight increase in luminosity, which gradually dies away as more carbon dioxide is introduced, until a non-luminous flame results, whilst if carbon dioxide, instead of air, be supplied to a Bunsen burner through the air holes, the luminosity is destroyed, and the flame has all the characteristic colour of the blue part of the inner zone.

It is a significant fact that Professor Smithells, in his second objection, considers the amount of acetylene present in a luminous flame insufficient to account for the light emitted, without taking the trouble to perform, or at any rate record, a single experiment in support of his unbelief.

The statement made by me, that just before luminosity commences 80 per cent. of the unsaturated hydrocarbons present at that spot consist of acetylene, is characterised as "likely to give a very false impression as to the importance to be attached to the presence of this gas," as Professor Smithells is at a loss to understand how a mixture of 1.5 per cent. of acetylene and 0.5 per cent. of other unsaturated hydrocarbons mixed with 98 per cent. of other gases, four-fifths of which are actually incombustible, could be supposed to have the properties I attribute to it.

If he means by this that the liberated carbon particles in the flame are not derived from the small quantity of acetylene, it seems hardly logical to suppose that they come from the 0.5 per cent. of other unsaturated hydrocarbons, and if they do not come from the unsaturated hydrocarbons at all, perhaps Professor Smithells will be able to explain their source.

If a mixture of 1.5 per cent. of acetylene with any combustible gas which gives a non-luminous flame was burnt from a jet no luminosity would be developed by the flame, and no trace of acetylene found at the top of the inner zone, it having been all consumed or polymerised before the temperature necessary for its decomposition was reached, but it is, nevertheless, a fact that 1.5 per cent. of acetylene, *present at the spot where luminosity usually commences*, will render such a flame luminous.

In an acetylene flame, the nitrogen and products of combustion diffusing into the flame dilute the acetylene present at the commencement of luminosity to 15 per cent. of the gases present at that point,

and the acetylene flame gives more than 10 times the light of the gas flame with its 1·5 per cent.

In an analysis made by me of the gases present in the non-luminous gas flame just before luminosity commences, I found 18·65 per cent. of combustible gas, whereas Landolt (*Pogg. Annalen*, 1856, 99, 389), in his experiments on the same portion of the flame, only found 10·01 per cent.

Gases present in the Inner Zone of Flame just before commencement of Luminosity.

	Lewes.	Landolt.
Hydrogen	2·35	2·59
Methane	7·80	0·79
Carbon monoxide.....	6·52	5·45
Unsaturated hydrocarbons..	1·98	1·18
	<hr/> 18·65	<hr/> 10·01

Landolt also notes the fact that the gas from the lower portion of the flame is free from smell, but that from the higher portions has a feeble empyreumatic odour.

I should have thought that the small proportion of combustible gases present at this point was an important proof that luminosity must be due to some such action as that to which I have ascribed it, rather than to any ordinary combustion.

In order to see if 1·5 per cent. of acetylene injected into the upper portion of the non-luminous zone of de-illuminated coal gas restored its luminosity, coal gas was slowly passed through washing flasks containing a solution of bromine in potassic bromide until its illuminating power was reduced to 1·7 candles. Two open tubes were then arranged side by side, and ordinary coal gas burnt from one, and de-illuminated coal gas from the other, in flames of equal size, and acetylene was then allowed to flow through a fine platinum tube into the inner zone of the de-illuminated gas flame, at such a rate as to form 1·5 per cent. of the gases present there, the result being that the flame became nearly as luminous as the one used for comparison.

Another point insisted upon by Professor Smithells is (3) that "there is no evidence of any local condition of temperature within the flame such as would point to the decomposition of acetylene with the evolution of much heat."

In order to see exactly what the increase of sensible heat at the moment of decomposition of pure acetylene amounted to, I arranged a thermo-couple in a small, hard glass tube, passed acetylene through the tube until free from air, and while the gas was burning at the exit of the tube, heated six inches of the tube in such a way that the

thermo-couple should be at the spot where the acetylene entered the heated zone. The luminous decomposition commenced, as is usually the case, about two-thirds of the way up the heated zone, and the glow slowly ran back to the commencement of the heated area, and on coming in contact with the thermo-couple gave a rise of temperature of 30° as the mean of three closely concordant experiments.

It is evident from this experiment, that no very high local condition of temperature would be found in the flame at the spot where the decomposition of the acetylene took place.

The fourth conclusion has been already fully dealt with.

In his fifth conclusion Professor Smithells says: "The conclusion in favour of the acetylene theory, based on the comparative luminosity of the ethylene and acetylene flames, is due to a neglect of the consideration that in the latter there are higher temperatures, and a greater relative amount of carbon."

When acetylene and ethylene are burnt at the same rate of flow from similar burners, a certain portion undergoes non-luminous combustion in order to supply the heat necessary to, in the one case, form acetylene and then decompose it, and in the other to decompose it only.

That far more ethylene is needed to do this work is manifest from the size of the non-luminous zone, which is many times greater than that of the acetylene flame.

The portion of the gas undergoing non-luminous combustion generates heat only, of which but little is radiated; the portion converted into acetylene and decomposed gives off its energy to a considerable extent by radiation, hence, although the heat of combustion of acetylene may be far higher than the heat of combustion of ethylene, it is conceivable that the acetylene flame may develop but little more heat than a flame of ethylene of the same size.

The figures I gave were for the interior of the flame only, and I quite agree that the outer envelope of the lower portion of an acetylene flame must be hotter than the same portion of an ethylene flame, but it by no means follows that the total heat developed by the acetylene flame is much greater than that developed by the ethylene. Ethylene and acetylene both contain two atoms of carbon in the molecule, and if we do not assume some such theory as the one proposed, we might be led into the error of supposing that the luminosity of the ethylene should be only one half that of acetylene, because the carbon is diluted with twice the volume of hydrogen, whereas experiment shows its illuminating value is only one quarter.

Professor Smithells argues, that because a platinum wire glows nearly as strongly in the lower portion of the outer envelope of an acetylene flame as the carbon particles within that envelope, that

the heat of the flame is sufficient to raise them to this high degree of incandescence. This assumption is apparently based on the idea that they both have equal powers of emitting light when heated to the same temperature, which is about as reasonable as supposing that carbon has the same emissive powers for light as the earths used in a Welsbach mantle.

It is also evident that the platinum wire must be heated to a higher temperature in the outer envelope of the flame than the carbon particles which are within it.

Metals at a high temperature have been shown to reflect light, and it is quite possible that some of the apparent brightness of the platinum wire is due to light reflected from its surface.

In arriving at his sixth conclusion, Professor Smithells has repeated an experiment described by me, and finds that "the indirect evidence deduced from the behaviour of cyanogen arises from the yellow ammonia flame having been mistaken for one containing solid carbon."

When a cyanogen flame issuing from a small jet has hydrogen supplied around it, the inner rose coloured cone becomes luminous, and on examining the light emitted, by means of a spectroscope, a continuous spectrum is obtained in which the nitrogen lines are faintly visible. If now the hydrogen be increased in quantity, the flame enlarges, the luminosity becomes fainter and more spread over the flame, and the light emitted no longer gives a continuous spectrum, but only the nitrogen lines.

If the flame emitting the continuous spectrum be now surrounded with oxygen, the luminous inner zone shrinks in size and emits an intense light, which gives a bright continuous spectrum with flutings which correspond to the cyanogen lines. This experiment is best performed with a burner made of three concentric platinum tubes, cyanogen being supplied to the central one, hydrogen to the middle, and oxygen to the outer tube.

Professor Smithells has repeated this experiment, but apparently has only dealt with the cyanogen flame in presence of a large excess of hydrogen, and, noting that the luminosity was low and of a yellowish colour, he attempted to deposit carbon from it upon a cold porcelain dish. Failing to do this, he then fed a hydrogen flame with ammonia, obtained a similar appearance in the flame produced, and on examining both flames with a spectroscope, got identical lines, which he says are those of ammonia; and from these facts he argues that in the above experiment an ammonia flame has been mistaken for one containing solid carbon.

These experiments I think are entirely fallacious. If a hydrogen flame be taken, and ethylene be passed into it until it is endowed with

the same or even far higher luminosity than the hydrogen flame fed with cyanogen, it is impossible to deposit carbon particles from it by immersing in the flame a cold porcelain surface, because the intense power which the excess of heated water vapour present in the flame has of oxidising the solid carbon particles is so great that no deposition is possible, and this result is therefore no proof of the absence of carbon particles.

The spectra given by the cyanogen and ammonia fed into hydrogen flames are unquestionably identical, and on comparing them with the spectrum of nitrogen given by a Geissler vacuum tube, they were found also to correspond with the spectrum given by this gas.

The evidence adduced by Professor Smithells to show that ammonia and not the carbon particles is the cause of luminosity is therefore of no value, and his assumption that the increased luminosity obtained when the dual flame is fed with oxygen is due to sodium vapour from the platinum is also absolutely devoid of foundation.

It is evident that in the experiment properly performed with hydrogen alone, we are dealing with temperatures only just sufficient to lead to luminosity, and a piece of cold metal placed against the inner cone causes it to again become non-luminous, whilst if hydrogen be replaced by carbon monoxide no luminosity ensues, a fact which might be taken to support Professor Smithells' views were it not that a slight increase of temperature leads to luminosity, as when the dual flame is surrounded with oxygen; whilst a still further increase in temperature not only again increases the luminosity, but enables one to obtain a copious deposit of carbon from the flame.

This is readily done by burning the cyanogen from the end of a tube and surrounding it with nitric oxide, the decomposition of this endothermic body (the heat of formation of which is -4575°) raising the temperature of the flame to a point at which the cyanogen burns with a dazzling light, and with the flow of cyanogen and nitric oxide properly regulated it can be made to deposit soot in abundance.*

The continuous spectrum given by this flame is of a most magnificent character, showing brilliant flutings in the red and green, and extending with particular brilliancy far into the violet, and when the light is developed from a burner of the kind before described, by using quartz lenses and prisms the spectrum may be projected upon a screen.

I think there can be no doubt from these experiments that I was perfectly correct in my former statement (*Proc. Roy. Soc.*, 1895, 57, 465) that the luminosity of a cyanogen flame is purely a question of temperature, whilst I have no doubt that, given sufficient heat to

* This soot contains a trace of paracyanogen. In order to obtain a deposit, the cyanogen and nitric oxide must be pure.

rapidly decompose it, as high an illuminating value as that of acetylene would be obtained.

The seventh conclusion arrived at by Professor Smithells is that "the theoretical arguments based on thermochemical considerations are invalid."

In my paper (*loc. cit.*, p. 451), I incautiously speak of carbon existing in a molecular state of division, meaning, as the context clearly shows, exceedingly small particles of solid carbon, but Professor Smithells does not fail to make the most of this slip, and supposes that it is a periphrasis for "carbon in the form of gas," and that if so it sounds the key note of much that follows, as, whilst I continue to speak of solid particles of carbon, my theoretical speculations are applicable only to atoms.

I am not aware that when atoms of carbon form molecules, a disappearance of heat takes place, and my general impression was that when gaseous matter assumed the solid form, heat was evolved rather than absorbed, and as these are the only factors which would invalidate my arguments, I fail to see what Professor Smithells means.

Moreover, I carefully point out in my paper (*loc. cit.*, p. 466) that I consider these theoretical calculations of "no value, except as showing that a ratio does exist between heat of formation and illuminating value."

Professor Smithells' last conclusion is "the phenomena of luminous hydrocarbon flames can be adequately explained without the acetylene theory." If by this it is meant that because an imperfect explanation already exists no one is to attempt to render our knowledge more exact, it seems to me so utterly opposed to the whole spirit of scientific inquiry that I think it best to ignore it, more especially as I fail to see how such an idea can be reconciled with the quotation from his own work with which Professor Smithells commences his paper, "A problem remaining to be studied concerns the exact course of the decomposition of the hydrocarbon in the flame."

In conclusion, I must protest against the statement made by Professor Smithells that I adduce measurements of temperature as the chief basis for the acetylene theory. I have clearly pointed out in the paper criticised that at most they are only valuable for comparison under well-defined conditions.

I consider the acetylene theory of luminosity in hydrocarbon flames to be based upon the following facts.

1. That the largest proportion of the unsaturated hydrocarbons in a gas flame are converted into acetylene before luminosity commences.
2. That acetylene develops luminosity when heated to a temperature at which it decomposes, the conditions under which this takes place rendering the presence of atmospheric oxygen impossible.

3. That the temperature necessary to decompose acetylene with luminosity is insufficient to raise the carbon liberated from it to the point at which it emits light.

4. That in luminous hydrocarbon flames of sufficiently high temperature the luminosity varies directly with the amount of acetylene present where luminosity commences.

Professor Smithells has not attempted to experimentally refute any one of these points, and until this is done I, at any rate, shall consider that the "acetylene theory" offers a satisfactory explanation of the most important phenomenon of luminous hydrocarbon flames.

I desire to express my thanks to Mr. A. Haddon, Demonstrator of Physics at the Royal Naval College, for the help he has afforded me in the work entailed by this paper.

XXV.—*Solution and Diffusion of certain Metals in Mercury.*

By W. J. HUMPHREYS.

(Communicated by J. W. MALLET.)

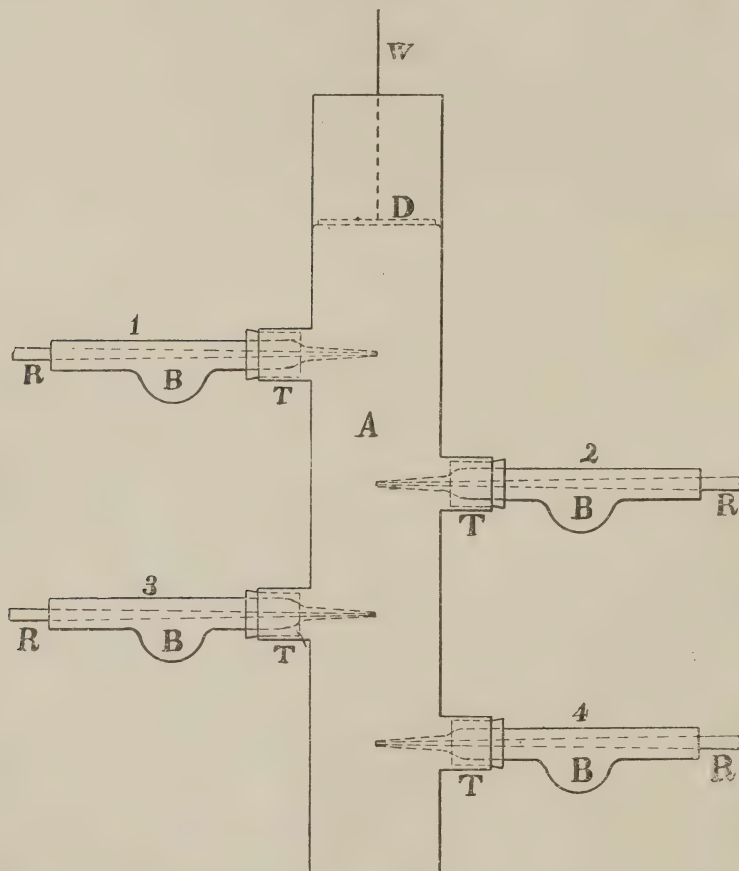
THE purpose of the investigation described in this paper was to examine quantitatively the solution and diffusion of metals in mercury, and thus to obtain some idea of the extent to which these phenomena differ, if at all, from solution and diffusion in the case of non-metallic solids in liquids.

Possibly this question has already been worked upon, and the results published, but if so, I have only to say that both search and inquiry have so far failed to inform me of the fact, and I therefore venture to publish my results, with the hope that, if not entirely new, they may nevertheless be of some value for the purpose of comparison with results already obtained.*

* Since this paper was written, my attention has been called to an article by the late Dr. F. Guthrie, "On Certain Molecular Constants" (*Phil. Mag.*, Nov., 1883, 16, 321). In the latter part of this paper, pages 329—339, Dr. Guthrie treats of the diffusion in mercury of sodium and potassium amalgams, and also of the diffusion of the pure metals, lead, tin, and zinc. In the case of lead, tin, and zinc, he allowed the diffusion to continue 31 days, and in each case made but a single series of analyses. His method of operation (differing entirely from mine) was to place the mercury with the metal to be examined in a burette of suitable size, and at the end of the diffusion to draw off slowly from the bottom of the burette the whole of the amalgam in, as nearly as possible, 13 equal portions. The temperature at which he allowed the diffusion to take place was 16° to 17° , from 10° to 12° lower than that at which I worked, consequently, only a general agreement in our results could be expected. However, on examining his table of results (p. 337 of his article), I find

The method of investigation was to fill an upright vessel of uniform horizontal cross section with pure mercury, place on its upper surface a piece of the solid metal to be examined (freshly amalgamated on the surface of contact), and after allowing it to remain in

FIG. 1.



that wherever our values for lead are nearly the same, his corresponding values for tin and zinc are approximately the same as the corresponding values I obtained for zinc and tin respectively.

Dr. Guthrie did not make his own analyses, but entrusted this part of the work to others, one of whom furnished the analyses of lead, a second those of tin, and a third those of zinc, and I think it not impossible that in transferring these analyses to his table of results, those of tin and zinc became interchanged. If so, his results and mine agree quite as closely as could be expected. This relation between our results makes a repetition of the investigation of the diffusion of tin and zinc very desirable.

contact with the mercury for a certain length of time in a place free from external disturbances, and of fairly constant temperature, to take, from definite depths below the surface, samples of the mercury, and examine them for the foreign metals carried down by diffusion.

The method of obtaining samples of the amalgam for analysis may be understood by reference to Fig. 1. A is a cylindrical glass vessel, 150 mm. high, and 25 mm. internal diameter, with four tubules T, 10 mm. in diameter. Corks were placed in the tubules, and through the corks were passed the tubes 1, 2, 3, and 4, to the centre of the tank A. The portion of each of these tubes entering the tank was drawn out rather small, so as to interfere as little as possible with the process of diffusion. The inner end of each tube was cut off perpendicularly to its axis, the opening thus produced being from 0.5—0.75 mm. in diameter; this opening was closed by a small, wooden rod R which could be easily put in place or removed by a slightly rolling motion. The tubes and the tank A were all rigidly bound to suitable framework, and the distances between the ends of the various tubes, as well as that between the end of the lowest tube and the bottom of the tank carefully measured. The tank A was then filled to a definite depth with pure mercury, the freshly amalgamated disk D of the metal to be examined put in position, and the whole allowed to remain quietly in a suitable place until the time came for removing the samples for analysis. The distances from the surface of the mercury to the end of the first tube, from the end of the first to the second, from the second to the third, from the third to the fourth, and from the fourth to the bottom of the tank, were each usually made equal to 25 mm.

The upper surface of the disk D was covered with sealing wax, so as to confine the action of the mercury to a known surface, that is, the under surface of the disk. A small wire W, usually fastened to the sealing wax, though occasionally soldered to the disk (in no case was any of the solder dissolved away), made it convenient to put the disk in position at the beginning of the experiment, and to remove it at the end.

The samples to be analysed were removed as follows. When the diffusion had proceeded as long as desired, the wooden rod in tube 1 was gently removed, and a sufficient amount (about 20 grams) of the amalgam collected in the side bulb B. This rod was then put back in place, and a similar process of drawing off the amalgam and replacing the rod, so as to prevent any further outflow of the amalgam, was employed in the case of the tubes 2, 3, and 4 respectively, and in the order named. The whole process for all four tubes generally required less than one minute. The mercury was then withdrawn

from the tank, and the tubes removed and emptied of their samples, which were carefully weighed and analysed.

A somewhat different variety of tank was also used; it was square, three sides and the bottom being of wood, and the fourth side of glass. Each side measured about 25 mm. inside. In this case, square, instead of circular, pieces of the metal were used. Two tanks of each variety were employed, and although no difference was found in their behaviour, they are, nevertheless, distinguished in the table of results. A and B refer to the wooden tanks of square cross section, whilst C and D refer to the glass ones of circular cross section.

The method of analysis adopted in the case of lead amalgam was to volatilise as much of the mercury as possible without loss of lead, dissolve the residue in dilute nitric acid, add an excess of sulphuric acid, and evaporate till fumes of sulphuric acid began to come off freely; then add water or dilute sulphuric acid till all the mercuric sulphate was dissolved, the sulphate of lead of course remaining undissolved. This was then collected, the sulphate of mercury removed by washing with dilute sulphuric acid, and the acid in turn by dilute alcohol; the sulphate of lead was then dried and weighed, and the percentage of lead in the amalgam estimated.

In the case of tin, zinc, and bismuth amalgams, as much as possible of the mercury was volatilised without loss of the dissolved metal, the residue dissolved in nitric acid, evaporated to dryness, and then strongly heated, so as to reduce the nitrate of tin, zinc, or bismuth to the corresponding oxide, and also to decompose and remove the mercuric nitrate; the oxide of the metal under investigation was then weighed, and its percentage in the amalgam calculated.

All the mercury was volatilised from the copper amalgams, the residue dissolved in nitric acid, evaporated to dryness and heated, and from the oxide thus obtained the copper and its percentage in the amalgam calculated. Although the copper in the amalgam never, with but one exception, amounted to as much as three parts in 100,000, nevertheless, as soon as the mercury began to distil off, the whole surface of the amalgam assumed first one, and then another, brilliant colour, some of these being repeated a second time, until finally it became and remained in appearance like a solid mass of copper.

The mercury was also completely distilled from the silver amalgams, and thus the silver obtained pure, and weighed as such.

As already stated, the temperature did not change very greatly during any one experiment, still it was not constant; when the time of diffusion was several days, the average temperature, as given in the table, was obtained by taking the average of the temperature, as shown by a thermometer kept beside the tank, at 9 A.M., and at

4 P.M. When the time of diffusion was less than one day, several readings of the thermometer were taken during the interval and averaged. After preparing a tank for a diffusion experiment, it was put in place, and the mercury allowed to come to a steady temperature before the amalgamated disk was put on it.

The results of the work are all given in the table, which needs no explanation, except possibly the statement that the decimals in the column headed "Percentage of metal" are probably in many cases carried further than the accuracy of the work would warrant. The last figure of course, was certainly never correct, but the third could usually be trusted, and since the work was done with care it was thought best to give the results as they appear in the table.

Two sets of curves (pp. 248 and 249) are plotted for each metal examined. Those to the left have for abscissæ the depths in millimetres below the surface of the points from which the samples were taken, and for ordinates the percentages of the metals found. These curves consequently represent the conditions of the columns of amalgam from top to bottom, as found after the diffusion had been going on for a definite length of time. The time, in days, of diffusion is marked on each of these curves. The other sets of curves, those to the right, have for ordinates the percentages of the metals found, and for abscissæ the time, in days, of their diffusion, and consequently they represent the rates of concentration at definite depths, that is, 25, 50, 75, and 100 mm. respectively below the surface.

Owing to the small extent to which silver and copper dissolve, their curves are plotted with ordinates respectively 10 and a 100 times greater than those of the curves of other metals; and their curves of concentration, those to the right, were so nearly coincident that it seemed best in each case to let a single curve represent all four.

A set of comparison curves for the different metals is given just below those of copper (Fig. 3). Those to the left give the conditions of the columns of amalgam at the end of 10 days' diffusion, whilst those to the right show the rates of concentration at a depth of 25 mm.

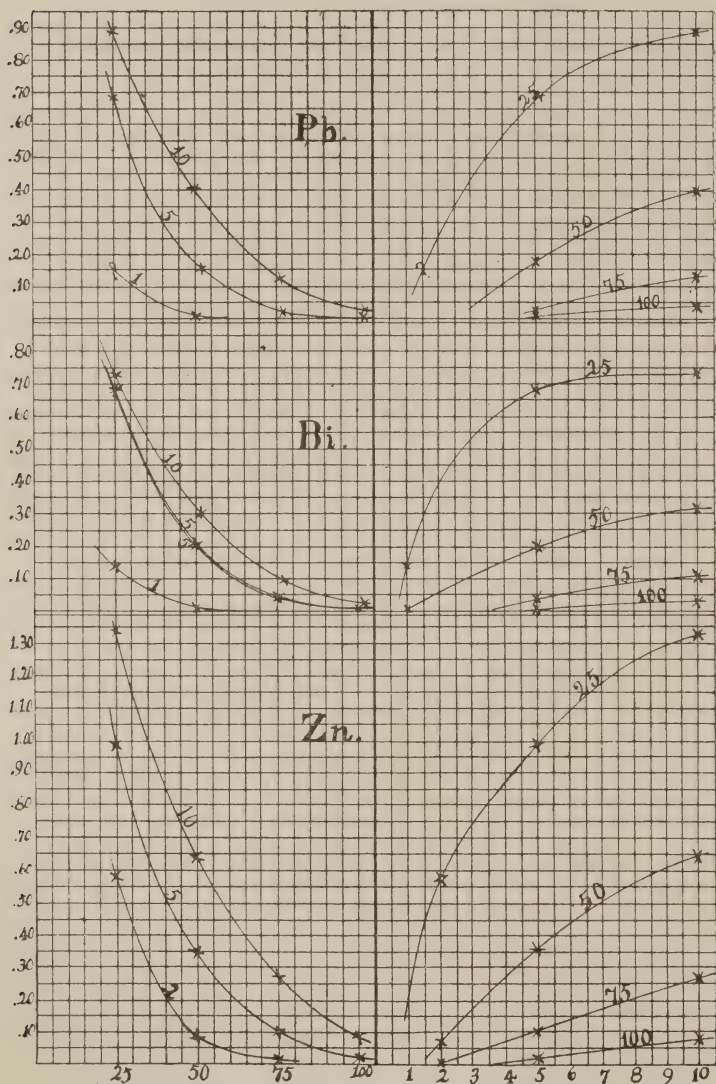
From the table and the curves it will be seen that, so far as these experiments go, solution and diffusion in this case are not essentially different from the same phenomena in the case of non-metallic solids and liquids.

Copper and silver are both interesting from the fact that they dissolve to a very slight extent (at ordinary temperatures), but diffuse very rapidly.

Not only did the mercury seem to become saturated with the silver from the fact that very little silver dissolved after the first day, and apparently none at all after the fifth, but also that, when the

amalgam obtained by five or 10 days' diffusion was allowed to cool down slowly, small crystals would separate out, but dissolve again in the amalgam from which they had separated on slightly warming it.

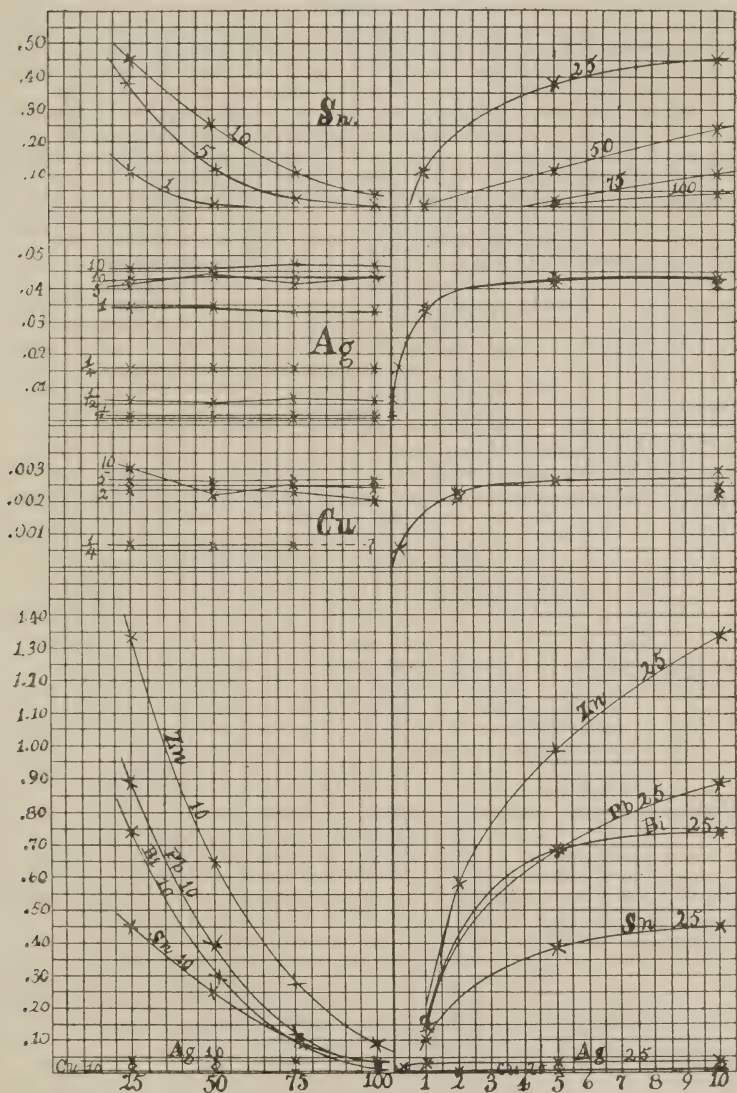
FIG. 2.



The extreme rapidity with which silver diffused led to the suspicion that possibly some form of amalgam was obtained of greater

density than that of mercury. To test this, a considerable amount (probably from 75 to a 100 grams) of saturated silver amalgam was carefully placed on a column of mercury and allowed to stand two

FIG. 3.



hours. Samples were then taken from the surface and from different depths and analysed. The results, as shown by the table, indicated

the same concentration from top to bottom, which disproved the idea that the rapidity was due to the formation of an amalgam heavier than the mercury; and, besides, no such silver amalgam has ever been obtained. It seems, therefore, safe to say that, whilst silver dissolves to a comparatively small extent in mercury, it diffuses through it with relatively great velocity, about 20 mm. per minute, which is fully 600 times as great as the velocity with which zinc diffuses.

This work was suggested to me by Dr. J. W. Mallet, F.R.S., of the University of Virginia, and was done there under his supervision during the months of July, August, and September, 1895, and I wish to thank him for his kindly and helpful assistance whenever any difficulty presented itself. I wish also to thank Professor Dunnington for occasional but always helpful and kind assistance.

Of course, the present paper is in the main simply preliminary, and I hope to be able at an early date to investigate the influence of temperature on the solution and diffusion of metals in mercury, and also to investigate the diffusion of mercury along solid bars of other metals.

I had hoped to examine the solution and diffusion in mercury of certain metals not given in the table, but was unable to do so because my work was interrupted at the end of September by other duties.

Table of Results.

Substance dissolved.	Time of diffusion.	Average temperature C.	Depth in millimetres of sample.	Percentage of metal.	Tank.	Remarks.
Pb	10 days	25·66°	25·0	0·7717	B	The method of withdrawing the amalgam in these two cases was different from that described and used in all the other cases, and as it was not very satisfactory, these two sets of results are not plotted.
"	"	"	49·0	0·3192	"	
"	"	"	75·0	0·0971	"	
"	"	"	101·0	0·0220	"	
"	5 days	25·30	25·0	0·5463	A	
"	"	"	48·5	0·1455	"	
"	"	"	74·0	0·0125	"	
"	"	"	100·0	0·0059	"	
"	10 days	28·16	25·0	0·8906	C	
"	"	"	49·5	0·4061	"	
"	"	"	76·0	0·1258	"	
"	"	"	102·5	0·0292	"	
"	5 days	29·87	25·0	0·6892	D	
"	"	"	52·0	0·1506	"	
"	"	"	76·5	0·0170	"	
"	"	"	101·5	0·0046	"	

Table of Results (continued).

Substance dissolved.	Time of diffusion.	Average temperature C.	Depth in millimetres of sample.	Percentage of metal.	Tank.	Remarks.
Pb	1 day	27.60	25.0	?	B	Lost by accident.
"	"	"	50.0	0.0026	"	
"	"	"	75.0	trace	"	
"	"	"	100.0	"	"	
Sn	10 days	27.54	25.0	0.4500	B	
"	"	"	48.5	0.2511	"	
"	"	"	75.5	0.1053	"	
"	"	"	99.5	0.0361	"	
"	5 days	29.10	24.5	0.3833	A	
"	"	"	50.5	0.1137	"	
"	"	"	76.0	0.0291	"	
"	"	"	101.0	0.0036	"	
"	1 day	27.60	25.0	0.1061	D	
"	"	"	50.0	0.0045	"	
"	"	"	75.0	none	"	
"	"	"	100.0	"	"	
Bi	10 days	27.18	25.0	0.7366	A	
"	"	"	51.5	0.3000	"	
"	"	"	77.5	0.0943	"	
"	"	"	102.0	0.0195	"	
"	5 days	27.49	25.0	0.6855	C	
"	"	"	50.0	0.2019	"	
"	"	"	75.0	0.0319	"	
"	"	"	100.0	0.0062	"	
"	"	28.29	25.0	0.6902	"	
"	"	"	50.0	0.2081	"	
"	"	"	75.0	0.0416	"	
"	"	"	100.0	0.0028	"	
"	1 day	27.60	25.0	0.1384	"	
"	"	"	50.0	0.0019	"	
"	"	"	75.0	none	"	
"	"	"	100.0	"	"	
Zn	10 days	27.55	25.0	1.3300	B	
"	"	"	50.0	0.6413	"	
"	"	"	75.0	0.2734	"	
"	"	"	100.0	0.0905	"	
"	5 days	26.87	25.0	0.9870	C	
"	"	"	50.0	0.3540	"	
"	"	"	75.0	0.0944	"	
"	"	"	100.0	0.0192	"	
"	2 days	27.50	25.0	0.5826	"	
"	"	"	50.0	0.0696	"	
"	"	"	75.0	0.0044	"	
"	"	"	100.0	none	"	
Cu	10 days	27.23	25.0	0.0031	A	
"	"	"	50.0	0.0022	"	
"	"	"	75.0	0.0025	"	
"	"	"	100.0	0.0024	"	
"	5 days	26.23	25.0	0.0027	"	
"	"	"	50.0	0.0026	"	
"	"	"	75.0	0.0027	"	
"	"	"	100.0	0.0027	"	

Table of Results (continued).

Substance dissolved.	Time of diffusion.	Average temperature C.	Depth in millimetres of sample.	Percentage of metal.	Tank.	Remarks.
Cu	2 days	29·4	25·0	0·0024	A	
"	"	"	50·0	0·0024	"	
"	"	"	75·0	0·0023	"	
"	"	"	100·0	0·0020	"	
"	6 hrs.	29·3	25·0	0·0007	"	
"	"	"	50·0	0·0007	"	
"	"	"	75·0	0·0007	"	
"	"	"	100·0	trace	"	
"	30 mins.	29·4	25·0	none	"	
"	"	"	50·0	"	"	
"	"	"	75·0	"	"	
"	"	"	100·0	"	"	
Ag	10 days	28·04	25·0	0·0462	D	Samples taken out at temperature 28·8°.
"	"	"	51·5	0·0460	"	
"	"	"	76·5	0·0483	"	
"	"	"	102·5	0·0461	"	
"	"	28·09	25·0	0·0424	B	Samples taken out at temperature 26·4°.
"	"	"	50·0	0·0439	"	
"	"	"	76·0	0·0433	"	
"	"	"	100·0	0·0434	"	
"	5 days	27·80	25·0	0·0415	D	Samples taken out at temperature 26·2°.
"	"	"	51·5	0·0450	"	
"	"	"	77·5	0·0423	"	
"	"	"	102·0	0·0432	"	
"	1 day	26·47	25·0	0·0349	C	
"	"	"	50·0	0·0344	"	
"	"	"	75·0	0·0335	"	
"	"	"	100·0	0·0332	"	
"	6 hours	27·86	25·0	0·0165	D	
"	"	"	50·0	0·0161	"	
"	"	"	75·0	0·0162	"	
"	"	"	100·0	0·0163	"	
"	2 hours	25·7	25·0	0·0060	C	
"	"	"	50·0	0·0052	"	
"	"	"	75·0	0·0074	"	
"	"	"	100·0	0·0061	"	
"	30 mins.	30·1	25·0	0·0026	D	Time of taking out all four samples, 30 secs.
"	"	"	50·0	0·0010	"	
"	"	"	75·0	0·0007	"	
"	"	"	100·0	0·0014	"	
"	5 mins.	27·15	25·0	0·0006	"	Time of taking out samples, 30 secs. Chloride formed and amount estimated by comparison with standard solution.
"	"	"	50·0	0·0006	"	
"	"	"	75·0	0·0006	"	
"	"	"	100·0	0·0006	"	
"	"	29·3	25·0	0·0006	C	Time of taking out samples, 22 secs. Estimated as above.
"	"	"	50·0	0·0006	"	
"	"	"	75·0	0·0006	"	
"	"	"	100·0	trace	"	

Table of Results (continued).

Substance dissolved.	Time of diffusion.	Average temperature C.	Depth in millimetres of sample.	Percentage of metal.	Tank.	Remarks.
Ag	30 secs.	29·6	50·0	none	C	The two samples drawn off simultaneously. Time, 5 secs.
"	"	"	100·0	"	"	
Silver amalgam	2 hours	25·7	0·0	0·0029	D	Not plotted.
"	"	"	25·0	0·0017	"	
"	"	"	50·0	0·0028	"	
"	"	"	75·0	0·0027	"	
"	"	"	100·0	0·0034	"	

XXVI.—*The Symmetrical Dimethylsuccinic Acids.*

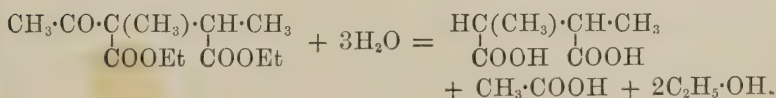
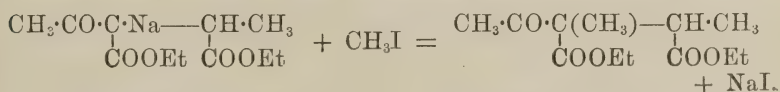
By WILLIAM ARTHUR BONE, and WILLIAM HENRY PERKIN, JUN.

INTRODUCTION.

IN 1869, Wislicenus (*Ber.*, 1869, 2, 720) described as dimethylsuccinic acid a substance which he had observed among the products of the reduction of iodopropionic acid by means of zinc dust. The substance itself was a syrup, which only partially crystallised on long standing, but it yielded a highly characteristic lead salt, which, on analysis, gave results corresponding with the empirical formula $C_6H_8PbO_4$.

Five years later, Weidel (*Annalen*, 1874, 173, 109), by the reduction of pyrocinchonic acid, $\begin{array}{c} CH_3 \cdot C \cdot CO \\ | \\ CH_3 \cdot C \cdot CO \end{array} > O$, by means of sodium amalgam, obtained a crystalline acid, melting at 170° , which could be sublimed, for the most part without change, and which he termed "hydropyrocinchonic acid."

In 1878, v. Hardtmuth (*Annalen*, 192, 142), working under the direction of Wislicenus, studied the action of methylic iodide on the sodium compound of ethylic β -methylacetosuccinate in benzene solution, and on hydrolysing, by means of alcoholic potash, the ethereal salt thus formed, obtained a "dimethylsuccinic acid" melting at 170° . The reactions involved in this process may be thus written



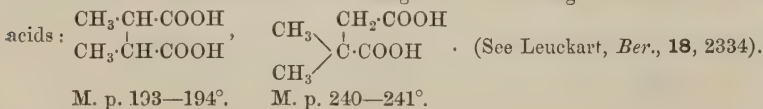
In 1882, v. Roser (*Ber.*, **15**, 2012) obtained "hydropyrocinchonic acid" by the reduction of pyrocinchonic acid by means of hydrogen iodide, and found that it melted at 190° . A very similar result was obtained by Weidel and Brix (*Monatsh.*, 1882, **3**, 612), who, however, used sodium amalgam as the reducing agent; the acid they obtained crystallised in glistening, triclinic needles, melting at 189° .

Three years later, Otto and Beckurts (*Ber.*, 1885, **18**, 825) published the results of a detailed investigation on the reduction of pyrocinchonic acid. When this acid was reduced by hydrogen iodide in sealed tubes at 220° , two acids were obtained, which could easily be separated by fractional crystallisation from water; the more insoluble acid melted at $193\text{--}194^{\circ}$, and seemed to be identical with the acids obtained by v. Roser and Weidel and Brix respectively, whilst the other melted at $118\text{--}120^{\circ}$. Quite different results were obtained when sodium amalgam was used as the reducing agent; in this case, in addition to the acid melting at $193\text{--}194^{\circ}$, there was produced an isomeric acid which melted without decomposition at $240\text{--}241^{\circ}$, whilst the acid melting at $118\text{--}120^{\circ}$ was not to be found among the products of reduction. This last experiment gave results, therefore, quite different from that in which hydrogen iodide was employed as the reducing agent, but, on repeating it, no trace of the acid melting at $240\text{--}241^{\circ}$ could be detected amongst the products, which, on the other hand, contained acids melting at $193\text{--}194^{\circ}$ and $118\text{--}120^{\circ}$.

An examination of the acid melting at $193\text{--}194^{\circ}$ showed that when it was heated to 200° it was transformed into an anhydride melting at $186\text{--}187^{\circ}$, which dissolved in hot water, and yielded, not the original acid, but the acid melting at $240\text{--}241^{\circ}$, which they found might be distilled without decomposition. They concluded, therefore, that these acids stood to one another in the same relationship as do fumaric and maleic acids, and they termed them dimethylsuccinic and isodimethylsuccinic acids respectively.*

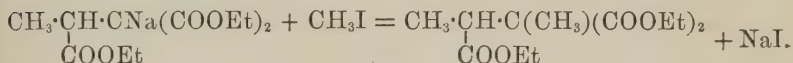
They found that when the acid melting at $118\text{--}120^{\circ}$ was heated to 160° , it decomposed with evolution of carbonic anhydride, and concluded that it was identical with the ethylmethylmalonic acid prepared in 1880 by Conrad and Bischoff (*Annalen*, **204**, 143, 162), which melt at 118° .

* Otto and Beckurts published their paper in 1885, two years before Wislicenus put forward his views as to the constitution of fumaric and maleic acids. From the views then held as to the constitution of the last-named acids, we may infer that Otto and Beckurts would have assigned the following constitutions to their



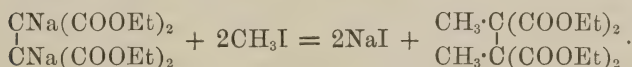
In 1886, Bischoff and Rasch (*Annalen*, **234**, 54) prepared a symmetrical dimethylsuccinic acid synthetically by three methods, which may be briefly described as follows.

1. By the action of methylic iodide on the sodium derivative of ethylic propenyltricarboxylate, according to the equation



The oil formed was hydrolysed by means of alcoholic potash, and the tricarboxylic acid thus obtained was heated at 160° until the evolution of gas had entirely ceased.

2. By hydrolysis of ethylic dimethylacetosuccinate (prepared by the action of ethylic α -bromopropionate on the sodium derivative of ethylic methylacetoacetate) by means of alcoholic potash.
3. By the action of methylic iodide on the disodium derivative of ethylic acetylenetetra-carboxylate, according to the equation



The oil formed was hydrolysed by means of potassium hydroxide, and the tetracarboxylic acid obtained was heated at 170° until the evolution of gas had entirely ceased.

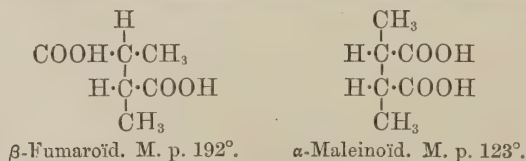
They found that the dimethylsuccinic acid obtained by either of these methods melted at 187°, and that on being heated to its melting point it lost water, and yielded an anhydride melting at 87°.

These results were fully confirmed by Leuckhart (*Ber.*, 1885, **18**, 2344), who prepared the acid synthetically from ethylic methylmalonate and ethylic α -bromopropionate. He found that it melted at 188—189°, and at that temperature was converted into an anhydride melting at 78—81°, which, with hot water, yielded, besides the original acid melting at 189°, an isomeride melting at 121—122°. The last-named acid, although it resembled in some respects, such as crystalline form and solubility, the acid melting at 118—120°, obtained by Otto and Beckurts by the reduction of pyrocinchonic acid, differed from it in that it might be distilled apparently without change. It will be observed that Leuckhart's results were quite incompatible with those of Otto and Beckurts; matters were, however, considerably cleared up in the following year, when Otto and Rössing published a remarkable paper (*Ber.*, 1887, **20**, 2737), which contained an entire refutation of the conclusions arrived at by Otto and Beckurts two years previously. They now found that their dimethylsuccinic acid melting at 193—194° is *not* changed, on heating to 200°, into an

anhydride melting at 186—187°, which with water yields "isodimethylsuccinic acid" melting at 240—241°, but, on the contrary, like Bischoff's dimethylsuccinic acid, it was converted into an anhydride melting at 86—87°, which with water yielded the original acid again. The acid, when treated with acetyl chloride, was converted into a mixture of two anhydrides, one of which melted at 86°, and the other at 38°, the last-named, with water, again yielding the original acid melting at 195°.

Further, they found that the acid melting at 121°, which Otto and Beckurts had obtained by the reduction of pyrocinchonic acid, did not decompose at 180° with evolution of carbonic anhydride, and, therefore, could no longer be considered as ethylmethylmalonic acid; on the contrary, it was converted by acetyl chloride into an anhydride melting at 87°, which with water yielded a mixture of two acids melting at 195° and 121° respectively. They concluded, therefore, that both these acids were dimethylsuccinic acids.

In 1888, Zelinsky (*Ber.*, 1888, **21**, 3160) prepared two symmetrical dimethylsuccinic acids by the hydrolysis of $\alpha\alpha$ -dimethylecyanosuccinate (obtained by the action of potassium cyanide on ethylic α -bromopropionate) by means of concentrated hydrochloric acid. One acid melted at 192°, and was almost insoluble in cold water; the other melted at 123—124°, and was fairly soluble in water. Both acids, on distillation, were transformed into the same anhydride, melting at 87°, which dissolved in water yielding the lower melting acid. He proposed the following constitutional formulæ for these acids:—



In 1890, Bischoff and Voit (*Ber.*, 1890, **23**, 639) reinvestigated these acids, their results in the main confirming those of Zelinsky. The two acids melted at 194° (para-acid) and 120° (anti-acid) respectively. At temperatures above 200°, both were converted into the same anhydride melting at 87°; this with water yielded a mixture of the para- and anti-acids. The para-acid, however, when heated with acetyl chloride, was converted into an anhydride melting at 38° (see Otto and Rössing), which with water yielded the para-acid again. On heating the anti-acid with concentrated hydrochloric acid at 180—190°, it was transformed into its isomeride.

In 1893, Crum Brown and Walker (*Annalen*, **274**, 41) prepared the symmetrical dimethylsuccinic acids by the electrolysis of potassium ethylic methylmalonate. They found that the para-acid melted

at 193° , and that its dissociation constant was $K = 0.0208$, whereas the anti-acid melted at $120-121^{\circ}$, and had the dissociation constant $K = 0.0138$.

The results of previous workers are given in tabular form on p. 258.

As the descriptions of the properties of the acids obtained by various experimenters differ so widely, the authors determined to carefully re-investigate the subject, with the results described in this communication.

They have prepared the symmetrical dimethylsuccinic acids in two ways, namely (1), by the hydrolysis of ethylic $\alpha\alpha$ -dimethylecanosuccinate with concentrated hydrochloric acid (Zelinsky's method), and (2) by the action of ethylic α -bromopropionate on the sodium derivative of ethylic methylmalonate, subsequently hydrolysing the product with alcoholic potash, and then heating the tribasic acid thus obtained at 200° until the evolution of carbonic anhydride had entirely ceased (Leuckhart's method). In both cases, the authors obtained a mixture of two symmetrical dimethylsuccinic acids, which were separated by fractional crystallisation from water. The melting points of these acids, especially that of the fumaroid (*trans*-) acid, differed materially from those assigned to them by previous investigators. When pure, the fumaroid (*trans*-) acid melts at 209° , and with acetyl chloride yields an anhydride melting at 43° , which by the action of water is reconverted into the *trans*-acid; it must, therefore, be the anhydride of this acid; further, this anhydride, on prolonged heating with acetic anhydride, is transformed into an isomeric anhydride melting at 88° , which, with water, yields the *cis*-acid.

The maleinoid (*cis*-) acid melts at 129° , and with acetyl chloride yields an anhydride melting at 88° , which with water is reconverted into the original acid, and must, therefore, be the anhydride of the *cis*-acid.

Both acids, when heated for a long time at 210° , or on distillation under atmospheric pressure, are converted into the *cis*-anhydride melting at 88° . Each of the anhydrides, when pure, yields with water only *one* acid (not a mixture of acids as stated by some previous investigators); that melting at 43° yields only the *trans*-acid melting at 209° , whilst that melting at 88° yields the *cis*-acid melting at 129° .

The authors have further shown that the *cis*-acid is almost entirely converted into the *trans*-acid when it is heated with concentrated hydrochloric acid in sealed tubes at 180° ; under similar conditions only a very small part of the *trans*-acid is transformed into the *cis*-modification, by far the greater portion of it being recovered unchanged.

Our results may be represented in tabular form as follows (p. 259).

Date.	Investigators and References.	Acids.	m. p. of acids.	Anhydride formation.	m. p. of anhydride.	Anhydride + water.
1869	Wislicenus (<i>Ber.</i> , 2 , 720).....	—	Liquid	—	—	—
1874	Weidel (<i>Annalen</i> , 173 , 109).....	"Hydropyrocinehonic acid"...	170°	—	—	—
1878	v. Hardtmuth (<i>Annalen</i> , 192 , 142)...	"Dimethylsuccinic acid".....	170°	—	—	—
1882	v. Roser (<i>Ber.</i> , 15 , 2012).....	"Hydropyrocinehonic acid"...	190°	—	—	—
1882	Weidel and Brix (<i>Monatsh.</i> , 3 , 612)...	"Hydropyrocinehonic acid"...	189°	—	—	—
1885	Otto and Beckurts (<i>Ber.</i> , 18 , 825).....	"Dimethylsuccinic acid"..... "Isodimethylsuccinic acid"..... "Ethylmethylmalonic acid".....	193—194° 240—241° 118—120°	Maintained at 200°	186—187°	"Isodimethylsuccinic acid," m. p. = 240—241°.
1885	Leuckhart (<i>Ber.</i> , 18 , 2344).....	Dimethylsuccinic acid.....	188—189°	At 200°	79—81°	Mixture of acids, m. p. 189° and 118—120°.
1887	Otto and Rössing (<i>Ber.</i> , 20 , 2737)....	Dimethylsuccinic acid.....	193—194° 121°	{ On heating to 200° With acetyl chloride With acetyl chloride	86—87° 38° 87°	195° acid. Do. Mixture of acids, m. p. 195° and 121°.
1888	Zelinsky (<i>Ber.</i> , 21 , 3160).....	α -maleinoid..... β -fumaroid.....	123° 192°	{ On distillation	87°	Maleinoid acid.
1890	Bischoff and Voit (<i>Ber.</i> , 23 , 639).....	Para..... Anti.....	192° 120°	{ At 200° Acetyl chloride At 200°	87° 38° 87°	Mixture of para- and anti- acids. Para-acid. Mixture of para- and anti- acids.
1893	Crum Brown and Walker (<i>Annalen</i> , 274 , 41)	Para..... Anti.....	193° 120—121°	{ —	—	—

Fumaroid (*trans*) acid.

M. p. = 209°.

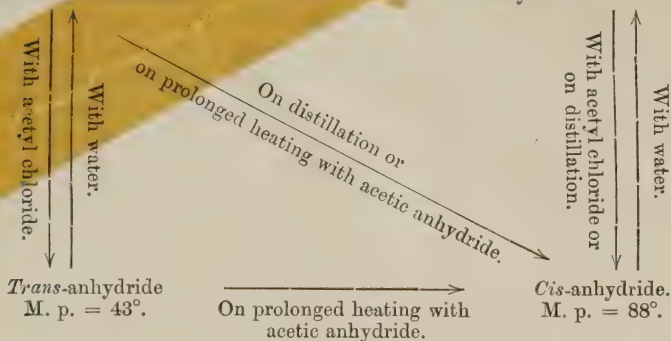
Insoluble in cold water.

With conc. HCl at 180°.

Maleinoid (*cis*) acid.

M. p. = 129°.

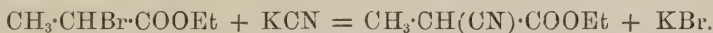
Fairly soluble in cold water.



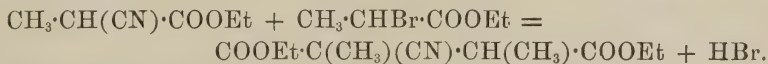
EXPERIMENTAL PART.

PART I.--A. *Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic α-Dimethylcyanosuccinate.*

The ethylic α-dimethylcyanosuccinate used in these experiments was prepared by the action of potassium cyanide on an alcoholic solution of ethylic α-bromopropionate, according to the method described by the authors in a previous paper (Trans., 1895, **67**, 420). The first action of potassium cyanide on ethylic α-bromopropionate consists in a replacement of the bromine by the cyanogen group, resulting in the production of ethylic α-cyanopropionate according to the equation



Subsequently a part of the ethylic α-cyanopropionate thus formed condenses with some of the unchanged ethylic α-bromopropionate, the result being the production of *ethylic αα-dimethylcyanosuccinate*, as follows.



The product, after distilling off the alcohol and extracting with ether in the usual manner, consists of a mixture of unchanged ethylic α-bromopropionate, ethylic α-cyanopropionate, and αα-dimethylcyanosuccinate, which are separated by careful fractionation under reduced pressure (30—40 mm.). The ethylic α-bromopropionate distils over between 77° and 85°, and the ethylic α-cyanopropionate between 103° and 110°, whilst the dark-coloured residue in the distilling flask consists for the most part of ethylic αα-dimethylcyanosuccinate. If the distillation be continued further,

a large quantity of a pale yellow oil passes over between 170° and 200° ; this oil was twice fractionated under a pressure of 80 mm., and the portion distilling between 195° and 200° was employed for the preparation of the symmetrical dimethylsuccinic acids.

Hydrolysis of the Oil.—The oil was mixed with about five or six times its bulk of concentrated hydrochloric acid in a large, round-bottomed flask, and to the mixture glacial acetic acid was added, until the oil just dissolved. The whole was then heated on a sand bath in a flask fitted with a long glass tube, ground into the neck to serve as a reflux condenser; when a sample of the liquid no longer deposited an oil on being diluted with water, it was allowed to cool, when a large crop of white crystals separated, consisting for the most part of ammonium chloride. The liquid was then poured into a large basin, and evaporated nearly to dryness, first over a bare flame, and finally on a water bath; water was added to the residue, and the solution again evaporated down in the water bath, this time completely to dryness. In this way, all the acetic acid and the ethylic acetate formed during the hydrolysis was got rid of. The residue was finally dissolved in hot water, when, on cooling, the solution deposited a greyish-white, crystalline mass of the crude acids; this was separated from the mother liquor by filtration at the pump, thoroughly washed with cold water, redissolved in hot water, boiled with animal charcoal, and filtered while hot. The filtrate, on standing, deposited a crop of white crystals, which, after drying, melted at $207\text{--}208^{\circ}$. After another recrystallisation from hot water, the substance melted at 209° . On concentrating the filtrate on the water bath, a further quantity of an acid was obtained on cooling; this acid, separated from the solution by filtration, and recrystallised, also melted at 209° . The filtrate was repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The thick, oily residue, which solidified on standing, was dissolved in hot benzene; the solution on cooling deposited crystals melting between 115° and 125° . These were once more crystallised from hot benzene, but no alteration in the melting point occurred; the acid was then dissolved in hot, concentrated, hydrochloric acid, and on cooling this solution crystals separated melting at $128\text{--}130^{\circ}$; after a second crystallisation from hot, concentrated hydrochloric acid, the substance melted at 129° .

The Acid melting at 209° (Trans-dimethylsuccinic acid).

This acid was analysed, with the following results, which agree well with the empirical formula $C_6H_{10}O_4$.

	Found.		Calculated.
	I.	II.	
Carbon.....	49·21	49·49	49·32
Hydrogen....	7·12	6·73	6·85

Trans-dimethylsuccinic acid is only very sparingly soluble in cold, but readily in boiling water. It is almost insoluble in benzene or chloroform, either hot or cold, but is fairly soluble in alcohol or ether.

Salts of the Acid.—To a neutral solution of the ammonium salt was added

- (a.) *Ferric chloride.* A reddish-brown precipitate of the ferric salt was immediately thrown down.
- (b.) *Copper sulphate.* A greenish-blue and very gelatinous precipitate was formed.
- (c.) *Lead nitrate.* A heavy, crystalline precipitate of the lead salt was produced; this was fairly soluble in hot water, and crystallised out again on cooling.
- (d.) *Silver nitrate.* A white precipitate of the silver salt was formed, fairly soluble in cold water.
- (e.) *Calcium chloride.* When calcium chloride was added to a dilute solution of the ammonium salt, no precipitate was produced either in the cold, or even on boiling for a considerable time. When, however, a fairly strong solution of the ammonium salt was used, the calcium salt was immediately precipitated, even in the cold.

We may here remark that the lead, silver, and calcium salts of the *trans*-acid, and especially the last-named, are decidedly more soluble than the corresponding salts of the *cis*-acid.

The Acid melting at 129° (Cis-dimethylsuccinic acid).

This acid was analysed, with the following results.

	Found.	Calculated for $C_6H_{10}O_4$.
Carbon.....	49·38	49·32
Hydrogen	6·88	6·85

Cis-dimethylsuccinic acid is fairly soluble in cold and readily in warm water, alcohol, or ether, separating rapidly from its aqueous solution when this is saturated with gaseous hydrogen chloride. It is more soluble in warm benzene and chloroform than the isomeric *trans*-acid.

Its salts are very similar to those of the *trans*-acid, but the calcium, lead, and silver salts are much less soluble in water than the corresponding salts of the *trans*-acid.

Separation of the Dimethylsuccinic Acids by means of their Calcium Salts.

The marked difference in the solubilities of the calcium salts of the *cis*- and *trans*-dimethylsuccinic acids affords a very convenient method of separating them, and of obtaining them readily in a state of purity. The method employed by the authors may be briefly described as follows.

Calcium chloride was added to a cold dilute solution of the ammonium salts of the two acids, when, after a short time, a white precipitate of the calcium salt of the *cis*-acid was formed; the whole was then gently warmed, and the precipitate collected with the aid of the pump, washed with a little hot water, and dissolved in hot concentrated hydrochloric acid. On cooling, crystals of the *cis*-acid, melting sharply at 129° , were deposited. The filtrate from the first crude precipitate was then concentrated on the water bath, and the small precipitate which separated during the operation, consisting of a mixture of the calcium salts, removed by filtration. On proceeding further with the concentration, a very bulky precipitate came down; this was separated from the mother-liquor with the aid of the pump and after washing with cold water, was dissolved in hot concentrated hydrochloric acid. On cooling, colourless crystals of the *trans*-acid melting at $204\text{--}209^{\circ}$ were deposited; after recrystallisation from water they melted at 209° .

B.—Preparation of the Symmetrical Dimethylsuccinic acids from Ethylic Methylmalonate and Ethylic α -Bromopropionate.

Forty-four grams of ethylic methylmalonate were mixed with a cold solution of 6 grams of sodium in 75 grams of absolute alcohol contained in a flask, and 45 grams of ethylic α -bromopropionate were carefully added. The mixture at once became hot, and sodium bromide began to separate. On heating the mixture in a water bath in a reflux apparatus for two hours, it became quite neutral; and on pouring the contents of the flask into water, a heavy oil separated. This was extracted with ether, the ethereal solution washed with dilute sodium carbonate solution and with water, dried over calcium chloride, the ether distilled off, and the dark-yellow, oily residue (60 grams) hydrolysed without further purification.

Hydrolysis of the Oil.—The oil was slowly added to about twice its weight of potassium hydroxide dissolved in alcohol, and contained in a large flask; there was a considerable development of heat, so that it was necessary to cool the flask well to prevent loss by frothing; the whole was then heated for six hours in a reflux apparatus on the water bath. A potassium salt soon separated, and after the conclusion of the hydrolysis, water was added to the liquid until this had dissolved,

the solution was poured into an evaporating basin, and concentrated on a water bath until all the alcohol had been driven off. The alkaline liquid was then cooled, carefully acidified with dilute hydrochloric acid, and repeatedly extracted with pure ether; the ethereal solution was dried over calcium chloride, the ether driven off, and the oil which was left heated in an oil bath at 200° until the evolution of carbonic anhydride entirely ceased. The oily residue was then dissolved in hot water, the solution boiled with animal charcoal, and filtered whilst hot; on cooling, the filtrate deposited a mass of white crystals, which were separated from the mother liquor by filtration, and washed well with cold water. On recrystallising these from hot concentrated hydrochloric acid, they melted at 209° ; a second recrystallisation from concentrated hydrochloric acid did not alter the melting point. This acid on analysis yielded the following results.

	Found.		Calculated for $C_6H_{10}O_4$.
	I.	II.	
Carbon.....	49.23	49.55	49.32
Hydrogen.....	6.75	6.92	6.85

and was identical in all its properties with the *trans*-acid melting at the same temperature obtained from ethylic $\alpha\alpha$ -dimethylecyano-succinate as described in the preceding section.

The filtrate, after removal of the acid melting at 209° was concentrated somewhat, and then repeatedly extracted with pure ether, the ethereal solution dried over calcium chloride, and the ether distilled off; a small quantity of a viscous oil was left, which, on standing, solidified almost entirely. This solid mass was ground up and washed with cold benzene to remove any oily matter, and the residue recrystallised from hot concentrated hydrochloric acid; in this way an acid was obtained melting at $125-127^{\circ}$, which, after a second recrystallisation, melted at 129° , and was identical in all its properties with the *cis*-acid melting at 130° obtained from ethylic $\alpha\alpha$ -dimethylecyanosuccinate. This acid on analysis yielded the following results.

	Found.	Calculated.
Carbon	49.30	49.32
Hydrogen	6.67	6.85

The amount of *cis*-dimethylsuccinic acid obtained by the method above described is comparatively small, not more than about one-fourth of the weight of the *trans*-acid formed at the same time.

Behaviour of the Dimethylsuccinic Acids on Prolonged Heating with Concentrated Hydrochloric acid in Sealed Tubes at 180° .

1. About 5 grams of the *trans*-dimethylsuccinic acid (m. p. 209°) were sealed up in a tube with about 40 c.c. of concentrated hydro-

chlorig acid, and heated at 180° for eight hours. On cooling, the crystals which had separated were collected, well washed with water, and dried at 100° ; they melted at $200\text{--}204^{\circ}$, and, after recrystallisation from water, at 208° . The mother liquor was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled off, when a very small quantity of an oily substance was left; this partially solidified on long standing, and the solid, after drying on a porous plate, was found to melt at $117\text{--}124^{\circ}$. It probably consisted of the *cis*-acid (m. p. 129°), but the amount was exceedingly small, nearly the whole of the *trans*-acid being recovered unchanged.

2. The *cis*-dimethylsuccinic acid (m. p. 129°) was heated in a tube with concentrated hydrochloric acid under pressure, as described in the previous experiment; the crystals which separated on cooling were collected, washed with water, and dried at 100° . They consisted of crude *trans*-dimethylsuccinic acid and melted between 190° and 200° , and, after recrystallisation from water, at $201\text{--}205^{\circ}$. The mother liquor was extracted with pure ether, and, as in the case of the previous experiment, a very small amount of the unchanged *cis*-acid was obtained.

Thus it is evident that, on heating the *trans*-acid under pressure with concentrated hydrochloric acid at 180° , it is only partially transformed into the *cis*-acid, the greater part of it being unchanged, and that when the *cis*-acid is subjected to the same treatment, it is for the most part converted into the *trans*-modification.

PART II.—THE ANHYDRIDES OF *Cis*- AND *Trans*-DIMETHYLSUCCINIC ACIDS.

A. Behaviour of the Dimethylsuccinic Acids on Prolonged Heating at $210\text{--}215^{\circ}$.

1. One gram of the *trans*-acid (m. p. 209°) was heated in a test-tube immersed in an oil bath, the temperature of which was raised fairly rapidly to about 170° , and afterwards gradually to 210° . At about 205° , the substance began to sublime without melting, and condensed on the upper and cooler portion of the tube in beautiful, asymmetric needles, which, after being spread on a porous plate, melted at $195\text{--}198^{\circ}$. When the temperature of the bath had risen to $210\text{--}211^{\circ}$, the substance melted, and water was given off; the bath was now kept at $210\text{--}215^{\circ}$ for half an hour, when the evolution of steam seemed to have ceased entirely. As the contents of the test-tube solidified on cooling, it was broken, and the solid mass spread on a porous plate; it was found to melt roughly between 65° and 85° . When treated in the cold with a dilute solution of sodium carbonate,

no effervescence could be detected, showing, therefore, that the acid had been completely converted into an anhydride. It was then dissolved in pure ether, and the ether allowed to gradually evaporate, when beautiful, colourless crystals were deposited melting at $84-86^{\circ}$, and identical with the anhydride prepared from the *cis*-acid by treatment with acetyl chloride. It dissolved readily in hot water, and after the solution had been cooled and saturated with gaseous hydrogen chloride, the *cis*-acid separated in crystals melting at $126-128^{\circ}$.

2. One gram of the *cis*-acid was subjected to the same treatment as has been described in the previous experiment; at a temperature rather above 200° , water was readily given off; the crude product solidified on cooling, and then melted between 70° and 80° . When treated with a cold, dilute solution of sodium carbonate, there was no evolution of carbonic anhydride, indicating that the transformation into anhydride was complete. The solid mass, which, after recrystallisation from absolute ether melted at 87° , was dissolved in hot water, the solution cooled, and saturated with gaseous hydrogen chloride, when the *cis*-acid separated in crystals melting at $128-129^{\circ}$.

Both the dimethylsuccinic acids, therefore, when heated at $210-215^{\circ}$, are converted into the *same* anhydride, which must be the anhydride of the *cis*-acid, as it yields this acid when treated with water.

B. Behaviour of the Dimethylsuccinic acids on Distillation at the Ordinary Atmospheric Pressure.

1. Two grams of the *trans*-acid were distilled in a small flask into which a thermometer was inserted; a heavy liquid came over between 230° and 235° , which solidified on cooling. The solid mass melted gradually between 70° and 82° , and when treated in the cold with a dilute solution of sodium carbonate, a small portion dissolved with effervescence, and from this solution a small quantity of an acid melting at about 195° was obtained. The anhydride, after treatment with sodium carbonate, and drying on a porous plate, melted at $83-86^{\circ}$, which was raised to 88° by recrystallisation from absolute ether. This anhydride, with water, yielded the *cis*-acid melting at $127-129^{\circ}$.

2. On distilling the *cis*-acid in the manner described in the previous experiment, a liquid passed over between 230° and 235° , which completely solidified on standing. The solid mass, which melted between 78° and 85° , showed no signs of effervescence when treated in the cold with a dilute solution of sodium carbonate, and, after recrystallisation from absolute ether, melted at 88° . When heated with water, it yielded the original *cis*-acid again.

Thus, on distillation under ordinary pressure, both acids are converted into the *cis*-anhydride; in the case of the *trans*-acid, however, the conversion is incomplete, a portion of the acid distilling over apparently unchanged.

C. *Distillation of the Trans-acid under Reduced Pressure.*

This experiment was undertaken with a view of ascertaining whether the *trans*-acid on distillation under reduced pressure would yield the same anhydride as it did when distilled under ordinary pressure; it was found, however, that it sublimed very readily under reduced pressure, and apparently for the most part unchanged. The sublimate dissolved very readily in dilute sodium carbonate with effervescence, but it had no constant melting point; a small portion melted at a temperature as low as 40° , but by far the greater part of it showed no signs of melting until the temperature had risen to 190° , when it gradually melted between 190° and 198° . It seems probable, therefore, that when the acid is sublimed under these conditions it is to a small extent converted into an anhydride, although we were unable to isolate a pure anhydride from the sublimate.

D. *Behaviour of the Acids on heating with Acetyl Chloride or Acetic Anhydride.*

1. About 5 grams of the *trans*-acid were mixed with about 7 c.c. of acetyl chloride, and the whole gently heated in a small reflux apparatus for 10 minutes, until the whole of the acid had just dissolved; it was then placed in a vacuum over solid potash, when the excess of acetyl chloride rapidly volatilised, leaving a yellowish-white crystalline mass, which was then dried on a porous plate in a vacuum. The crude product had no constant melting point, part melted between 30° and 40° , but quite half of it did not melt until the temperature had risen to 160° , indicating that a considerable portion of the original acid had remained unchanged. It was accordingly mixed with more acetyl chloride, and heated gently in a reflux apparatus on a sand bath for half an hour; the product, isolated as described above, now melted sharply at 43° . The substance was then heated for about 20 minutes in a reflux apparatus on a sand bath with acetic anhydride, the excess of acetic anhydride distilled off under reduced pressure, and the liquid residue placed in a vacuum over solid potash, where, after standing several days, it solidified to a pure white mass; this was spread out on a porous plate and left in a vacuum over solid potash, after which it melted very sharply at 43° .

The substance was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$.
Carbon	55.82	56.25
Hydrogen	6.48	6.25

On dissolving this anhydride in hot water, and cooling the solution, white crystals separated, which, after drying on a porous plate, melted at 208° , and were in all respects identical with *trans*-dimethylsuccinic acid. The substance melting at 43° is, therefore, the anhydride of *trans*-dimethylsuccinic acid.

2. Five grams of the *trans*-acid were mixed with 15 grams of acetic anhydride, the whole heated on the sand bath for three hours in a reflux apparatus, and then fractionally distilled under a pressure of 30 mm.; after the greater part of the acetic anhydride had come over, the temperature rose rapidly to 160° , when the receiver was changed, and the portion distilling over between 160° and 180° collected separately, and placed in a vacuum over solid potash. After the substance had become solid, the crystals were dried on a porous plate in a vacuum, when they melted between 40° and 50° , mostly, however, in the neighbourhood of 43° . A portion of the substance was treated in the cold with a dilute solution of sodium carbonate, but not the slightest effervescence could be detected, showing that no free acid was present. This anhydride was again heated with acetic anhydride for three hours, and the treatment described above repeated. Finally we obtained the *cis*-anhydride melting at 88° , which with water yielded the *cis*-acid melting at 129° .

From this experiment, it seemed probable that the *trans*-acid, when heated with acetic anhydride, yields first of all its own anhydride (m. p. = 43°), but that on prolonged heating with acetic anhydride this is converted into the *cis*-anhydride melting at 88° . This conclusion was confirmed as follows: A small portion of the *trans*-anhydride melting at 43° , obtained in D 1, was heated for several hours with acetic anhydride in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. After several days, the liquid deposited crystals, which when dried in a vacuum on a porous plate, were found to melt at 87 – 88° , and with water yielded the *cis*-acid.

Thus the *trans*-anhydride, on prolonged heating with acetic anhydride, is converted into the *cis*-anhydride.

3. Five grams of the *cis*-acid were heated with acetic anhydride for three hours on a sand bath in a reflux apparatus, the excess of acetic anhydride distilled off under reduced pressure, and the residual liquid placed in a vacuum over solid potash. On long standing, the liquid crystallised, and the crystals, after drying on a porous plate, melted at 87° , and on being dissolved in hot water yielded the *cis*-acid melting at 128 – 129° .

The *cis*-anhydride (m. p. 88°) was analysed with the following results.

	Found.	Calculated for $C_6H_8O_3$.
Carbon	55.99	56.25
Hydrogen	6.60	6.25

4. The *cis*-acid was dissolved in a slight excess of acetyl chloride, the solution gently warmed on the sand bath in a reflux apparatus for 20 minutes, and placed over solid potash in a desiccator, which was then exhausted; the acetyl chloride was thus rapidly volatilised, and the residue crystallised on standing. The crystals, after drying in a vacuum on a porous plate, were found to consist of the *cis*-anhydride melting at 88° .

Owens College, Manchester.

XXVII.—*Note on the $\alpha\alpha_1$ -Dimethylglutaric acids.*

By WILLIAM ARTHUR BONE and WILLIAM HENRY PERKIN, Jun.

In a paper published last year (Trans., 1895, **67**, 416), the authors described as $\alpha\alpha_1$ -dimethylglutaric acids two acids melting at 127° and 105 — 107° respectively, obtained, together with trimethylsuccinic acid (m. p. 152°), by the hydrolysis of the product of the action of ethylic α -bromisobutyrate on the sodium derivative of ethylic α -cyano-propionate, in alcoholic solution. In the same communication, they stated that Auwers and Thorpe (*Ber.*, 1895, **28**, 623) had shown that the acid melting at 105 — 107° was not a homogeneous substance, but a mixture in molecular proportion of *cis*- and *trans*- $\alpha\alpha_1$ -dimethylglutaric acids, melting at 127° and 140 — 141° respectively, but up to the time of the publication of their results the authors have not been able to confirm this opinion. Since that time, however, Auwers and Thorpe have published fuller details of their work (*Annalen*, 1895, **285**, 310), and the authors have accordingly subjected the acid in question to a further examination, with the result that they are able to substantiate the conclusions of these investigators.

The acid melting at 105 — 107° is in many respects a remarkable substance; it may be recrystallised from various solvents, such as benzene or concentrated hydrochloric acid, without any change in its melting point. The authors fractionally crystallised the normal calcium salt, obtained by adding excess of calcium chloride to a dilute solution of the ammonium salt, and on regenerating the acids from the successive fractions by separately dissolving them in concentrated hydrochloric acid, they were found to melt within 2° of the original

acid. No separation could be effected by this method. Auwers and Thorpe found, however, that if the acid calcium salt, prepared by adding the calculated quantity of calcium carbonate to an aqueous solution of the acid, was fractionally crystallised, two calcium salts could be obtained, one being very much less soluble than the other. On regenerating the acids, the more insoluble salt yielded *trans*-dimethylglutaric acid, melting at 140—141°, and the other *cis*-dimethylglutaric acid, melting at 127°.

The authors are able to confirm this result, and have resolved the acid, melting at 105—107°, into its two constituents, by the following method, also due to Auwers and Thorpe; it depends on the fact that *cis*-dimethylglutaric acid readily yields an anhydride on treatment with acetyl chloride, whilst the *trans*-acid remains unchanged. The acid, melting at 105—107°, was mixed with half its weight of acetyl chloride in a test-tube, the mixture gently warmed for about 10 minutes, until the evolution of hydrogen chloride had ceased, and the substance had completely dissolved, and the solution was then left in a vacuum over solid potassium hydroxide, until the whole of the acetyl chloride had volatilised. The solid residue thus obtained was quickly washed with benzene, whereby the anhydride of the *cis*-acid was completely removed, leaving behind the unchanged *trans*-acid, which, after recrystallisation from hot, hydrochloric acid, was found to melt at 140—141°. On leaving the filtrate in a warm place until the benzene had evaporated, an oily liquid was left, which, on long standing, became semi-solid; it dissolved readily in hot, concentrated hydrochloric acid, and on cooling the solution crystals of *cis*-dimethylglutaric acid, melting at 125—127°, separated. The mother liquor was extracted with pure ether, and after drying the ethereal solution over calcium chloride and distilling off the ether, a residue was left, which was recrystallised from benzene; in this way a small quantity of an acid, melting between 100° and 110°, was obtained. On grinding together equal portions of *cis*- and *trans*-dimethylglutaric acids in a mortar, a substance was obtained which had an almost constant melting point, namely, 104—108°, resembling in every way the acid melting at 105—107°, which the authors described in their former paper.

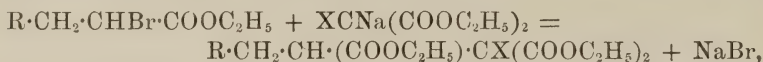
Owens College, Manchester.

XXVIII.—*Cis- and trans-Methylisopropylsuccinic acid.*

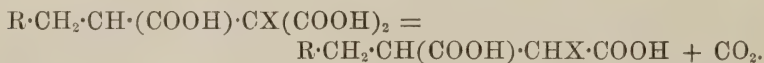
By WILLIAM HENRY BENTLEY, WILLIAM HENRY PERKIN, jun., and
JOCELYN FIELD THORPE.

THE action of the ethereal salts of α -bromo-acids of the fatty series on the sodium compounds of ethylic malonate and its derivatives may take place in two different ways.

1. The action may proceed directly with the simple separation of sodium bromide, thus:—



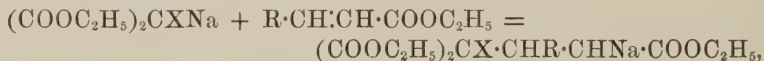
forming an ethereal salt of a tribasic acid, which, on hydrolysis and subsequent elimination of CO_2 , yields a derivative of succinic acid, thus:—



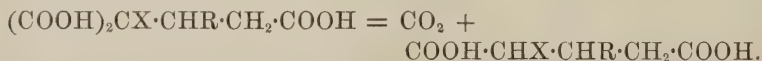
2. The reaction is an indirect one. In this case an unsaturated ethereal salt is first produced by the removal of hydrogen bromide,



and this unsaturated ethereal salt then condenses with the sodium derivative employed, as follows,



yielding a sodium derivative of an ethereal salt from which the corresponding tribasic acid may be isolated by hydrolysis. This tribasic acid then readily decomposes on heating with formation of a derivative of glutaric acid,



The direction in which the action proceeds depends generally on the conditions of the experiment; thus, when ethylic α -bromisubtyrate is digested with ethylic methyl malonate in alcoholic solution (Bischoff and Mintz, *Ber.*, 1890, **23**, 649), an ethereal salt of the formula $(\text{COOC}_2\text{H}_5)_2\text{C}(\text{CH}_3)\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$ is produced, from which, by hydrolysis and elimination of CO_2 , the two symmetrical dimethylglutaric acids are obtained; whereas if the experiment be performed in xylene solution at 200° , the action proceeds directly with separation of sodium bromide and formation of ethylic trimethylethanetricarboxylate, $(\text{COOC}_2\text{H}_5)_2\text{C}(\text{CH}_3)\cdot\text{C}(\text{CH}_3)_2\cdot\text{COOC}_2\text{H}_5$,

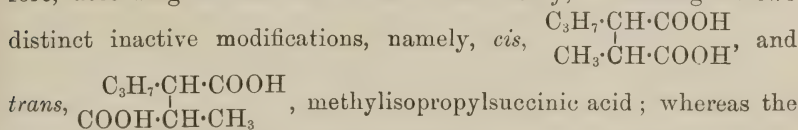
from which trimethylsuccinic acid is readily produced (Bischoff, *Ber.*, 1891, **24**, 1078; Bredt and Helle, *Inaugural Dissert.*, Bonn, 1893, 31; Auwers, *Annalen*, 1895, **285**, 260 and 301).

During some experiments on the action of ethylic bromomethylisopropylacetate, $(\text{CH}_3)_2\text{CH}\cdot\text{CBr}(\text{CH}_3)\cdot\text{COOC}_2\text{H}_5$, on the sodium derivative of ethylic malonate, on which one of us has been engaged for some time, it was found to be exceedingly difficult to decide whether the substances obtained were derivatives of succinic, or of glutaric acid,* and, in order to throw some light on this point, a series of experiments on the action of the next lower homologue, namely, ethylic bromisopropylacetate (ethylic α -bromisovalerate) on the sodium derivative of ethylic methylmalonate were instituted, with the results described in this communication.

If this decomposition proceed as indicated in equation 1, the end product would be methylisopropylsuccinic acid,



if, however, hydrogen bromide were eliminated, and subsequent condensation took place, the end product would be trimethylglutaric acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}(\text{CH}_3)\cdot\text{COOH}$, and it would be easy to distinguish between these substances, since, in the former case, the acid would contain two asymmetric carbon atoms, and be capable, therefore, according to the Le Bel-van't Hoff theory, of existing in two distinct inactive modifications, namely, *cis*,



trans, methylisopropylsuccinic acid; whereas the above trimethylglutaric acid, containing only one asymmetric carbon atom, is capable, according to the same theory, of existing in one inactive modification only.

The action of ethylic α -bromisovalerate on the sodium derivative of ethylic methylmalonate was first carried out in boiling xylene solution in the usual manner, the purified ethereal salt obtained was hydrolysed, and the acid produced heated at 200° until all evolution of carbonic anhydride had ceased.

From the product, two well characterised acids melting at $174\text{--}175^\circ$ and $124\text{--}125^\circ$, were isolated, which, from the study of their behaviour, were clearly shown to be stereoisomeric; these acids, therefore, are evidently the *cis*- and *trans*-methylisopropylsuccinic acids, which are formed by the direct action of ethylic α -bromisovalerate on the sodium derivative of ethylic methylmalonate, according to equation 1.

Cis-Methylisopropylsuccinic acid differs from the *trans*-acid in being

* It is hoped that the results of these experiments, which are complete, will be ready for publication shortly.

readily volatile with steam when heated with a 50 per cent. solution of sulphuric acid. It melts at 125—126°, and, when treated with hydrochloric acid, is partially converted into the *trans*-modification melting at 174—175°. When heated with acetic anhydride, or when distilled, the *cis*-acid yields a liquid anhydride, and this, on treatment with water, is reconverted into the original acid.

The *cis*-anilic acid,
$$\begin{array}{c} (\text{CH}_3)_2\text{CH}\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{CH}_3\cdot\text{CH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5 \end{array} \text{ (?)}, \text{ melts at } 160^\circ,$$
 and is different from the anilic acid of the *trans*-acid, although both yield the same anil when heated at 200°.

Trans-methylisopropylsuccinic acid is much less soluble in water than the *cis*-acid; it melts at 174—175°, and when heated with hydrochloric acid at 180°, is partially converted into the *cis*-acid.

When distilled under reduced pressure, or heated with acetic anhydride, the *trans*-acid yields a solid anhydride melting at 46°, which by treatment with water is reconverted into the same acid. If, however, this anhydride be boiled in a reflux apparatus for some time under ordinary pressure, and then distilled, the distillate is found to consist of the *cis*-anhydride; the conversion of the *trans*- into the *cis*-acid being complete under these circumstances. The *trans*-anhydride, on treatment with aniline, gives the anilic acid of the *trans*-acid, and this, when heated at 200°, yields the anil of the *cis*-acid.

We next studied the action of ethylic α -bromisovalerate on the sodium derivative of ethylic methylmalonate in alcoholic solution, and in this case again, curiously enough, working up the product in the way described in the body of the paper, we were only able to isolate *cis*-methylisopropylsuccinic acid, the *trans*-modification which should have been formed being apparently converted into the *cis*-acid under the conditions of hydrolysis employed in this particular instance.

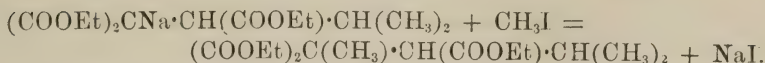
Lastly, in order that there might be no doubt as to the constitution of these acids, we have prepared them in the following way.

In the first place, the sodium derivative of ethylic malonate was digested with ethylic α -bromisovalerate, when a good yield of an ethereal salt was obtained, which has already been described by Roser (*Annalen*, 1883, **220**, 277), and which is undoubtedly ethylic isopropylethanetricarboxylate, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}(\text{COOC}_2\text{H}_5)\cdot\text{CH}(\text{COOC}_2\text{H}_5)_2$. In order to be certain of the constitution of this ethereal salt, it was hydrolysed, and the tribasic acid formed heated at 200°, whereby it was converted into isopropylsuccinic acid,



a result which confirms Roser's experiments.

The ethylic isopropylethanetricarboxylate was now treated with sodium and methylic iodide in alcoholic solution,

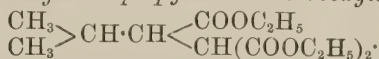


The ethereal salt thus formed was identical with that obtained in the previous experiments, since, on hydrolysis and subsequent elimination of carbon dioxide, a mixture of acids was obtained from which *cis*- and *trans*-methylisopropylsuccinic acid, melting at 174—175° and 124—125° respectively, were readily isolated. These acids differed in no respect from those produced in the manner previously described.

The latter method gives by far the best yield of these acids; it is therefore placed first in this paper, and described in most detail.

EXPERIMENTAL PART.

I. *Ethylic Isopropylethanetricarboxylate*,



In preparing this substance, 23 grams of sodium were dissolved in 250 grams of absolute alcohol and 160 grams of ethylic malonate added, when the sodium derivative separated as a white, gelatinous precipitate. The flask containing the mixture was then connected with a reflux condenser, heated on the water bath, and 209 grams of ethylic α -bromisovalerate added in small portions at a time to the boiling solution. The action was not violent, although sodium bromide separated immediately on adding the bromisovalerate; the boiling was continued for three hours, after which the product was neutral. The alcohol was, as far as possible, distilled off, this being most quickly and completely effected by placing the flask in the boiling water bath, bumping being prevented by suspending a piece of string from the neck of the flask, so as to hang in the boiling liquid.

When the alcohol had ceased to come over, the residue in the flask was mixed with water, the oil separated, the aqueous liquor extracted four times with ether, the ethereal solution dried over calcium chloride, and the ether distilled off. The oily product was then fractionated under reduced pressure (37 mm.); a small portion boiled below 200°, but the chief portion came over between 180° and 182°. The weight of this fraction was 186 grams, or 66 per cent. of the theoretical yield of ethylic isopropylethanetricarboxylate.

0.1510 gave 0.3209 CO_2 and 0.1155 H_2O . $\text{C} = 57.96$; $\text{H} = 8.49$.

$\text{C}_{14}\text{H}_{24}\text{O}_6$ requires $\text{C} = 58.33$; $\text{H} = 8.33$ per cent.

In order to prove that this ethereal salt has the constitution represented by the formula at the head of this section, 20 grams of the

pure substance were hydrolysed by boiling with an alcoholic solution of potash for two hours, evaporating the product three times with water, acidifying, and extracting several times with ether; after drying over calcium chloride and evaporating the ether, the oily acid was heated at 200° until the evolution of gas had ceased, and the product, which rapidly solidified and melted indefinitely at $90-110^{\circ}$, was recrystallised from hydrochloric acid until the melting point became constant at $116-117^{\circ}$.

0.2297 gave 0.4408 CO_2 and 0.1555 H_2O . $\text{C} = 52.33$; $\text{H} = 7.53$.

$\text{C}_7\text{H}_{12}\text{O}_4$ requires $\text{C} = 52.52$; $\text{H} = 7.52$ per cent.

A careful examination of this acid proved conclusively that it is identical with the isopropylsuccinic acid obtained by Hlasiwetz and Grabowski (*Annalen*, 1868, **145**, 207), from the fusion of camphoric acid with potash, and which Roser (*Annalen*, 1883, **220**, 272) has shown to be identical with the acid obtained by the hydrolysis of ethylic isopropylacetosuccinate with potash,



Not only do the melting points of these acids coincide, but on comparing the anilic acid produced from the acid obtained by us with that prepared from a sample of isopropylsuccinic acid, which had been obtained by fusing camphoric acid with potash, they both melted at 145° , and were identical in all respects.

This anilic acid, which does not appear to have been previously prepared, is readily obtained by mixing isopropylsuccinic anhydride with aniline in benzene solution; it crystallises from a mixture of light petroleum and ethylic acetate in large, glistening plates melting at 145° . A nitrogen determination gave the following figures.

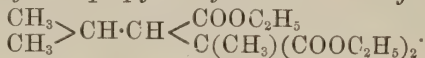
0.1991 gave 9.9 c.c. moist nitrogen at 12° and 760 mm. $\text{N} = 6.00$.

$\text{C}_{13}\text{H}_{17}\text{NO}_3$ requires $\text{N} = 5.96$ per cent.

On heating this anilic acid in a sulphuric acid bath at 200° for half an hour, it loses water, and is converted into the anil.

This compound crystallises from light petroleum ($80-100^{\circ}$) in microscopic needles melting at 213° . The same substance was obtained both from the anilic acid prepared from the synthetically produced isopropylsuccinic acid, and from that prepared from the isopropylsuccinic acid from camphoric acid.

Ethylic Isopropylmethylethanetricarboxylate,



This was prepared as follows. 13.3 grams of sodium were dissolved in 133 grams of absolute alcohol, and 166 grams of ethylic

isopropylethanetricarboxylate added; the mass became yellow, but no separation of the sodium derivative was observed. The flask was fitted with a reflux condenser, the solution cooled, and 95 grams (an excess) of methylic iodide added in small portions at a time through the condenser tube; the action was very violent, the temperature rising rapidly until the liquid boiled vigorously. In order to complete the action, the mixture was heated on the water bath for two hours, when it was found to be neutral; the product was then treated as usual, the alcohol being distilled off, water added, and the oil extracted with ether. This oil, which was deep red, owing to the presence of free iodine, was fractionated under reduced pressure (80 mm.), when the principal portion distilled between 200° and 210° ; the weight of this fraction was 144 grams, or 83 per cent. of the theoretical quantity. An analysis gave the following results.

0.2197 gave 0.4818 CO_2 and 0.1707 H_2O . $\text{C} = 59.81$; $\text{H} = 8.63$.

$\text{C}_{15}\text{H}_{26}\text{O}_6$ requires $\text{C} = 59.60$; $\text{H} = 8.60$ per cent.

Hydrolysis of Ethylic Isopropylmethylethanetricarboxylate by means of Alcoholic Potash.

The pure ethereal salt (144 grams) was boiled in a reflux apparatus with an alcoholic solution of one and a half times the calculated quantity of potash for four hours, the product diluted with water, and evaporated on a water bath to a small bulk until quite free from alcohol. On acidifying this potassium salt with hydrochloric acid, it was noticed that there was a marked evolution of carbon dioxide, which indicated that the tribasic acid, which should result from the direct hydrolysis of the ethereal salt, had either during the hydrolysis or on acidifying with hydrochloric acid, been at least partially decomposed into dibasic acids with loss of carbon dioxide, and this was afterwards found to be the case. On standing, an oil, which rapidly solidified, separated on the surface of the strongly acid liquid. The whole was then transferred to a separating funnel and extracted seven times with pure ether, the ethereal solution dried over calcium chloride, filtered, and evaporated, when a slightly yellowish oil remained, which partially solidified on standing. This product was heated in an oil bath at 200° , but only a small quantity of carbon dioxide was evolved, confirming the conclusion arrived at above, that the tribasic acid had been for the most part already decomposed. The light brownish residue which contained *cis*- and *trans*-methylisopropylsuccinic acids was then treated by the method described in the next paragraph.

Separation of cis- and trans-Methylisopropylsuccinic acid.

Method I.—The method used by us for the separation of these

acids is similar to that employed by Hell (*Ber.*, 1877, **10**, 2229) for the isolation of diisopropylsuccinic acid and of tetramethylsuccinic acid, namely, distillation in steam from a 50 per cent. solution of sulphuric acid.

The mixed acids were placed in a conveniently large flask, together with a 50 per cent. solution of sulphuric acid, and distilled in a current of steam, when a large quantity of an oil heavier than water passed over; at the end of two hours, as no more oil passed over and the distillate was only slightly acid, the distillation was stopped.

(a.) *Treatment of the Residue in the Distilling Flask.*—On cooling, a large quantity of a crystalline substance separated from the dark brown sulphuric acid solution; this was collected, and after being washed with water, it melted roughly at 130—160°; crystallisation from water, however, at once raised the melting point to 160—170°, and subsequently to 174—175°, where it remained constant; the quantity of this substance was 18 grams.

The filtrate from the crystals was extracted four times with ether, and the ethereal solution dried and evaporated; the thick, syrupy residue had only partially solidified after standing over sulphuric acid for two days in a vacuum; on treatment with cold benzene, this was readily separated into two parts.

1. An *insoluble*, white, crystalline mass melting roughly at 89—104°.

2. A *soluble* portion which was deposited as an oil on evaporating the benzene; the quantity of this was, however, small, and as all attempts to obtain a crystalline substance from it were unsuccessful, it was not further investigated. It is worthy of remark, however, that on dissolving this oil in water and saturating the solution with gaseous hydrogen chloride, the substance was reprecipitated as an oil, and not in a crystalline condition.

In order to purify the crystalline substance insoluble in cold benzene, it was treated with boiling benzene and filtered from a small quantity of insoluble inorganic matter; on cooling, needle-shaped crystals separated which, after being washed with benzene, melted at 95—110°, but, on repeated recrystallisation from water, the melting point rose to 117—118°, where it remained constant.

The quantity of this acid, which was evidently isopropylsuccinic acid, was only about 1 gram.

(b.) *Treatment of the Substance Volatile with Steam.*—The steam distillate consisted of a large volume of liquid containing oily drops at the bottom, which dissolved on the addition of excess of potash and warming; the clear solution thus obtained was evaporated in a porcelain dish to a small bulk, acidified with hydrochloric acid,

extracted six times with ether, and the ethereal solution dried over calcium chloride and evaporated, when a very small quantity only of an oil was left which solidified on standing; on recrystallisation from water, an acid was obtained melting at 174° — 175° , evidently identical with the acid of the same melting point already obtained as described above; the quantity was, however, very small and hardly sufficient for a melting point determination.

Considering the large quantity of original acid employed, only small amounts of pure substance had been extracted by ether, and it seemed likely, therefore, that an acid was contained in the steam distillate, which, owing to its great solubility in water, was not capable of being easily extracted by agitation with ether; this proved to be the case, for on evaporating the mother liquor (which had previously been made alkaline by the addition of potash) to dryness on the water bath, adding excess of concentrated hydrochloric acid, and again extracting six times with ether, a large quantity of a solid substance was obtained melting at about 110 — 120° . This could not be recrystallised in the ordinary way owing to its great solubility; but when it was dissolved in a little water, and the solution saturated with hydrogen chloride, the pure substance, on standing, separated almost completely in microscopic needles melting at 125 — 126° . The yield of this acid was 30 grams from the 144 grams of ethylic methylisopropylethanicarboxylate used.

The products of the hydrolysis of the 144 grams of this ethereal salt may therefore be tabulated as follows.

1. An acid (18 grams) melting at 174 — 175° , only very slightly volatile with steam,* insoluble in hot benzene.
2. An acid (1 gram) melting at 117 — 118° , not readily volatile with steam,* but easily soluble in hot benzene.
3. An acid (30 grams) melting at 125 — 126° , volatile with steam,* and readily soluble in hot benzene.

In the following sections, we give a detailed account of the properties of the two acids melting at 175° and 126° respectively, showing that the former is the *trans*-, the latter the *cis*-methylisopropylsuccinic acid.

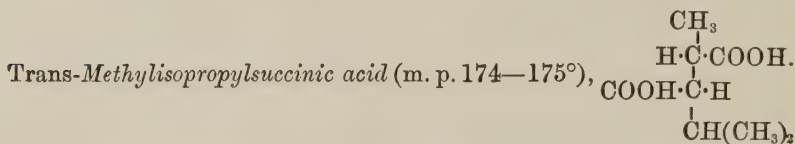
Method II.—Although as a method for the rough separation of large quantities of the crude mixed acids, distillation with steam from a 50 per cent. solution of sulphuric acid serves admirably, and yields the *cis*- and *trans*-acids in a tolerably pure form, yet it cannot be advantageously applied when smaller quantities have to be dealt with.

Repeated recrystallisation of the crude mixture of acids from water fails to produce an acid of higher melting point than 170 — 173° ,

* From a 50 per cent. solution of sulphuric acid.

and it is therefore almost impossible by these means to obtain a pure *trans*-acid; if, however, the recrystallised product be boiled for a few minutes with benzene, in which it is almost insoluble, filtered while hot, washed with warm benzene, and the product thus obtained subsequently recrystallised from water, long, flat needles of constant melting point, 174—175°, are readily obtained.

Owing to the marked difference in the solubility of the *cis*- and *trans*-acids in water, the *cis*-acid is obtained in a very fair degree of purity on saturating the mother liquors with hydrogen chloride; the product, however, still contains traces of the *trans*-modification, but can easily be purified by treating with cold benzene, filtering, evaporating the filtrate to dryness, and recrystallising the residue thus obtained from hydrochloric acid, as above described.



This acid crystallises from water in long, flat needles, which melt at 174—175°, and decompose at 190° with formation of the anhydride. The following results were obtained on analysis.

0.2272 gave 0.4587 CO₂ and 0.1640 H₂O. C = 55.00; H = 8.02.

C₈H₁₄O₄ requires C = 55.17. H = 8.04 per cent.

Trans-methylisopropylsuccinic acid is readily soluble in hot water, ether, and ethylic acetate, but only sparingly in light petroleum and chloroform, almost insoluble in cold water and benzene. The solubility in water was determined by Victor Meyer's method, when it was found that at 18°, 2.6146 grams of water dissolve 0.170 gram of the acid, or 100 parts of water dissolve 0.64 part of the acid at 18°. This acid is, therefore, very sparingly soluble in cold water.

The *silver salt*, C₈H₁₂O₄Ag₂, prepared by neutralising a 10 per cent. solution of the acid with a slight excess of ammonia, boiling for some time, concentrating, adding a little water, and then the requisite quantity of silver nitrate solution, gave the following result on analysis.

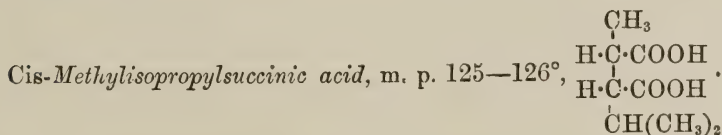
0.2122 gave, on ignition, 0.1181 Ag. Ag = 55.65.

C₈H₁₂Ag₂O₄ requires Ag = 55.67 per cent.

Action of Heat on trans-Methylisopropylsuccinic acid.—When gently boiled for a few minutes under slightly diminished pressure, and then distilled, *trans*-methylisopropylsuccinic acid is converted into an anhydride which, on boiling with water, yields an acid melting from 120—165°, and from which a small quantity of *trans*-acid can

be isolated by crystallisation from water. The mother liquor, when concentrated and saturated with hydrogen chloride, yields a considerable quantity of *cis*-methylisopropylsuccinic acid melting at 125—126°. The presence of the *trans*-acid in this product was at first thought to be due to its having distilled unchanged, but as no carbon dioxide was evolved on heating the distillate with a solution of sodium carbonate, this did not seem probable. Subsequently it was proved, however, that anhydrides of both acids exist, the *trans*-anhydride being only completely converted into the *cis*-modification after repeated distillation under ordinary or slightly reduced pressure.

Behaviour of trans-Methylisopropylsuccinic acid on heating with Hydrochloric acid at 180°.—In order to investigate this important point, 3 grams of the pure acid were heated with concentrated hydrochloric acid in a closed tube, at 180°, for eight hours; the crystals which separated on cooling, melted at 120—150°, but on recrystallising and extracting with hot benzene, a quantity of the *trans*-acid, melting at 174—175°, was readily obtained, whilst the mother liquor, on saturation with hydrogen chloride, yielded the *cis*-acid, the two acids being in, apparently, about equal proportions. As, on subsequent investigation, the *cis*-acid, when heated in like manner with hydrochloric acid, yielded a mixture of the two acids, it was inferred that here, as in the cases of the symmetrical $\alpha\alpha$ -dimethylglutaric acids, the hexahydroisophthalic acids, and other similarly constituted acids, a state of equilibrium exists. It is interesting to note that in this case it is quite easy to separate the mixture of the *cis*- and *trans*-acids obtained into its components by means of benzene; and that it does not behave like the mixture of *cis*- and *trans*-dimethylglutaric acids, which can only be separated with very great difficulty (*Annalen*, 1895, 285, 332).



On saturating the aqueous solution of the acid with hydrogen chloride and allowing it to cool, microscopic needles separate, which melt at 125—126°, and decompose at 140°, with formation of the anhydride. The analysis gave the following figures.

0.1135 gave 0.2282 CO₂ and 0.0794 H₂O. C = 54.83; H = 7.77.

C₈H₁₄O₄ requires C = 55.17; H = 8.04 per cent.

Cis-Methylisopropylsuccinic acid is readily soluble in all the usual solvents, with the exception of light petroleum, in which it is only

sparingly soluble in the cold; it also dissolves readily in acetyl chloride. The solubility in water, determined by Victor Meyer's method, yielded the following result at 18° . 2.1046 grams of water dissolve 0.0934 gram of the acid, or 100 parts of water dissolve 4.43 parts of the *cis*-acid at 18° , it is, therefore, much more soluble than the *trans*-acid, of which 100 parts of water dissolve only 0.64 part at this temperature.

The *silver salt*, $C_8H_{12}Ag_2O_4$, prepared by the same method as that employed in the case of the *trans*-acid, gave the following result on analysis.

0.2210, on ignition, gave 0.1232 Ag. $Ag = 55.74$.

$C_8H_{12}O_4Ag_2$ requires $Ag = 55.67$ per cent.

Action of Heat on cis-Methylisopropylsuccinic acid.—When gently boiled under reduced or ordinary pressure for a few minutes, or when slowly distilled, the acid readily loses water, and is converted into its own anhydride, and this, on boiling with water, again yields the *cis*-acid in a very pure condition. On treating a drop of this anhydride with a solution of sodium carbonate, on a watch glass, there is no evolution of carbon dioxide, so that the conversion is complete.

The Anhydrides of cis- and trans-Methylisopropylsuccinic acids.

Anhydride of trans-Methylisopropylsuccinic acid.—The simplest method of preparing this anhydride seemed to be the following. Five grams of the pure *trans*-acid were boiled with acetic anhydride for about two hours in a reflux apparatus, the solution poured into a glass dish, and the acetic anhydride evaporated as far as possible in a vacuum over potash. As no crystals separated after the lapse of five days, the product was distilled under reduced pressure (20 mm.), the anhydride passed over at 140 — 145° as a colourless oil, which, on standing, gradually solidified; it was pressed on a porous plate, and recrystallised from light petroleum (b. p. 80 — 100°), when it gave long, silky needles melting at 46° .

0.2010 gave 0.4520 CO_2 and 0.1534 H_2O . $C = 61.33$; $H = 7.70$.

$C_8H_{12}O_3$ requires $C = 61.54$; $H = 7.69$ per cent.

On boiling with water for half an hour, this anhydride dissolves, and, on cooling, the *trans*-acid separates in a very pure form, showing that the anhydride is in reality that of the *trans*-acid. The anhydride is not changed on distillation under reduced pressure, and even when rapidly distilled at the ordinary pressure it is only partially converted into the *cis*-modification. If, however, it be heated for a few minutes in a reflux apparatus and then distilled, it is converted

into the anhydride of the *cis*-acid, as shown by its yielding this acid on boiling with water, as also by its giving no precipitate with a benzene solution of aniline (see below).

The Anhydride of cis-Methylisopropylsuccinic acid.—This anhydride was prepared in the following manner. Five grams of the *cis*-acid were heated with acetic anhydride for two hours, and the solution placed over potash in a vacuum. As soon as the smell of acetic anhydride was no longer perceptible, the product was distilled under reduced pressure (25 mm.) when the anhydride passed over at 138—140° as a colourless oil; this, however, showed no signs of solidification, even when kept for a considerable time, and all subsequent efforts to procure it in a crystalline form proved fruitless. This anhydride, therefore, appears to be liquid at the ordinary temperature. An analysis of a sample which has been distilled under reduced pressure gave the following results.

0.1902 gave 0.4273 CO₂, and 0.1333 H₂O. C = 61.27; H = 7.78.

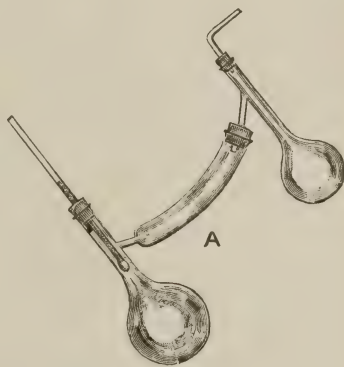
C₈H₁₂O₃ requires C = 61.54; H = 7.69 per cent.

On boiling with water for half an hour, this anhydride dissolves, and on saturating the solution with hydrogen chloride, the *cis*-acid melting at 125—126° is obtained in a pure state.

Conversion of the Anhydride of the trans-acid into that of the cis-acid.

Three grams of the *trans*-anhydride were heated to boiling for three minutes under ordinary pressure in a flask shaped as shown in the figure, the flask being inclined, so that the liquid could constantly run back; the flask was then placed in a horizontal position, and the anhydride distilled into the receiver A under reduced pressure.

The liquid thus obtained showed no signs of solidification after prolonged standing, and, as it yielded the pure *cis*-acid on boiling with water, it is evident that a transformation of the *trans*- into the *cis*-modification had actually taken place under the conditions of the experiment.



The Anilic acids and the Anil of cis- and trans-Methylisopropylsuccinic acids.

(1) *The Action of Aniline on the trans-Anhydride.*—Two grams of this anhydride were dissolved in benzene, and a molecular proportion of

aniline, also dissolved in benzene, added; a thick, white precipitate separated immediately, the contents of the beaker becoming solid. The product was then collected, washed with benzene, dried, and recrystallised twice from dilute alcohol; the slender silky needles thus obtained melted at 160° , and decomposed at 170° with evolution of bubbles of steam. The substance dissolves readily in sodium carbonate solution.

A nitrogen determination of this compound and its behaviour on hydrolysis proved that it consisted of the anilic acid of *trans*-methyl-isopropylsuccinic acid of the formula

$$\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\overset{\text{(CH}_3)_2\text{CH}\cdot\text{COOH}}{\underset{\text{CH}\cdot\text{CH}_3}{\text{C}}} \quad (?)$$

0.2590 gave 12.3 c.c. moist nitrogen at 17° and 753 mm. $\text{N} = 5.45$.

$\text{C}_{14}\text{H}_{19}\text{NO}_3$ requires $\text{N} = 5.62$ per cent.

Hydrolysis with Alcoholic Potash.—About 1 gram of this anilic acid was heated with alcoholic potash for 12 hours on a water bath; on evaporating, acidifying, and extracting with ether, an acid was obtained which melted at 160 — 170° , rising to 174 — 175° after treatment with hot benzene. It consisted, therefore, of the *trans*-acid, the formation of which proves conclusively that the substance described above is in reality the *trans*-anilic acid.

(2) *The action of Aniline on the cis-Anhydride*.—On mixing a solution of 1 gram of the *cis*-anhydride dissolved in benzene with a benzene solution of a molecular proportion of aniline, no precipitate of the anilic acid was formed as in the case of the *trans*-anhydride, so that this difference in behaviour towards a benzene solution of aniline may be used as a ready means of identifying these anhydrides. On evaporating to dryness on the water bath, an oil was left which only solidified after standing two days in a vacuum, and repeatedly stirring; on grinding this up with cold benzene, filtering and washing with benzene, a white powder was left which crystallised from dilute alcohol in large, prismatic needles melting sharply at 153° and decomposing at 160° . Thinking that perhaps this might be the same substance as the anilic acid obtained from the *trans*-anhydride (m. p. 160°), it was again recrystallised, but the melting point remained constant. A nitrogen estimation yielded the following figures.

0.2410 gave 11.9 c.c. moist nitrogen at 16° and 750 mm. $\text{N} = 5.71$.

$\text{C}_{14}\text{H}_{19}\text{NO}_3$ requires $\text{N} = 5.62$ per cent.

On hydrolysis with alcoholic potash, this substance yielded again the pure *cis*-acid, showing that it is in reality the anilide of the *cis*-acid.



The two anilic acids described above, when heated above their melting points, yield the same anil.

The Anil obtained from the trans-Anilic acid.—The *trans*-anilic acid was heated in a small test-tube in a sulphuric acid bath at 200° , until water ceased to be given off. On cooling, the anil remained as a thick, oily substance, which did not solidify on stirring, but it did so immediately on boiling with dilute ammonia. The insoluble matter was collected, washed with hot ammonia, and recrystallised from dilute alcohol, with the aid of animal charcoal. It is necessary to use a large quantity of the solvent, and to promote crystallisation by adding a crystal of the substance, otherwise owing to its low melting point and the higher temperature of the solvent, it frequently separates as an oil. This anilide crystallises in glistening plates melting at 85° ; it is insoluble in soda.

The Anil obtained from the cis-Anilic acid.—On heating this acid in the manner described, an anil was obtained, identical in melting point and crystalline form with that prepared from the *trans*-acid. A nitrogen estimation was made.

0.1136 gave 5.5 c.c. moist nitrogen at 16° and 759 mm. $\text{N} = 5.74$.

$\text{C}_{14}\text{H}_{17}\text{NO}_2$ requires $\text{N} = 6.06$ per cent.

Salts of cis- and trans-Methylisopropylsuccinic acids.

In each case a 10 per cent. solution of the inorganic salt was added to a 10 per cent. solution of the ammonium salt of the acid.

	126° <i>cis</i> -	175° <i>trans</i> -
CuSO_4 .	<i>Cold</i> , no precipitate	The same.
„	<i>Hot</i> , no precipitate; but on cooling, the copper salt separates in flakes	„
$\text{Pb}(\text{NO}_3)_2$.	<i>Cold</i> , white crystalline precipitate..	„
„	<i>Hot</i> , „ „ „	„
$\text{Hg}_2(\text{NO}_3)_2$.	<i>Cold</i> , white precipitate	„
„	<i>Hot</i> , soluble in excess	„
HgCl_2 .	<i>Cold</i> , no precipitate	„
„	<i>Hot</i> , „ „ „	White crystalline precipitate.
CaCl_2 .	<i>Cold</i> , no precipitate	„
„	<i>Hot</i> , „ „ „	„
Fe_2Cl_6 .	<i>Cold</i> , flocculent red-brown precipitate	„
„	<i>Hot</i> , „ „ „	„

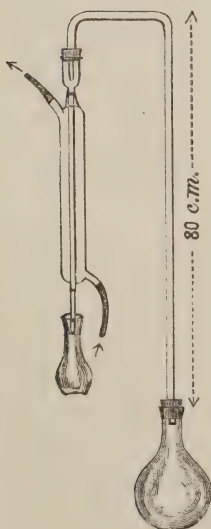
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The Action of Ethylic α -Bromisovalerate on the Sodium Compound of Ethylic Methylmalonate in Alcoholic Solution.

The action of ethylic α -bromisovalerate on the sodium compound of ethylic methylmalonate was next investigated, in order to determine whether by this means the acids described above, or, perhaps, different ones, would be formed.

Six grams of sodium were dissolved in 60 grams of absolute alcohol, the solution mixed with 43 grams of ethylic methylmalonate, and 53 grams of ethylic α -bromisovalerate added in small quantities at a time to the hot solution; a tolerably energetic action set in, and after three hours' heating on a water bath, the mass was found to be neutral. The alcohol was then distilled off, the product mixed with water, the oil which was deposited separated, and the aqueous liquid extracted six times with ether; after drying over calcium chloride, the ether was distilled off, and the residual oil fractionated under diminished pressure (67 mm.), when the chief fraction distilled between 190° and 210° ; the quantity was, however, only 10 grams, or not more than 15 per cent. of the theoretical yield.

Hydrolysis of this Ethylic Salt.—The ethereal salt was hydrolysed by boiling with a 50 per cent. solution of sulphuric acid in a round-



bottomed flask, connected with Bischoff's reflux apparatus, and heated on a sand bath. As during the operation an acid oil distilled over with the alcohol, and collected in the receiver, a short Liebig's condenser was placed on the shorter arm of the apparatus, as shown in the figure, so as to ensure complete condensation, and from time to time the oil which had distilled was separated and returned to the flask. After three hours' boiling, all the oil had disappeared, and as, on adding water to the liquid, it dissolved without the separation of oily drops, the hydrolysis was considered as complete. The product was now distilled with steam, and, as in the previous experiment (p. 276), it was noticed that an oily substance distilled over first, and sank to the bottom of the receiver; at the end of two hours the oil ceased to come over, and as the distillate was only faintly acid, the distillation was stopped.

As no crystalline substance separated from the sulphuric acid solution on cooling, it was extracted with pure ether, and the ex-

tract, after drying, evaporated. The oil which was left did not solidify even when left in a vacuum over sulphuric acid for five days; it was therefore dissolved in water and the solution saturated with hydrogen chloride, but the substance was reprecipitated as an oil, no crystals being formed. The steam distillate, which contained, as stated above, an insoluble oil, was made strongly alkaline, evaporated to dryness on the water bath, mixed with excess of concentrated hydrochloric acid, and extracted with ether. The oily product, which solidified partially on standing, was dissolved in water and saturated with hydrogen chloride; the crystalline substance which separated melted at $113\text{--}117^\circ$, but after repeated recrystallisations it had a constant melting point of $125\text{--}126^\circ$.

An analysis gave the following figures.

0.2303 gave 0.4639 CO_2 and 0.1643 H_2O . C = 54.94; H = 7.93.

$\text{C}_8\text{H}_{14}\text{O}_4$ requires C = 55.17; H = 8.04 per cent.

The substance is therefore without doubt *cis*-methylisopropylsuccinic acid.

It is remarkable that in this reaction the *cis*-acid alone should be produced; no trace of the *trans*-acid could be isolated, and it could hardly have been overlooked, as it usually separates with great ease, and is readily purified.

Action of Ethylic α -Bromisovalerate on the Sodium Derivative of Ethylic Methylmalonate in Xylene Solution.

As explained in the introduction, the object of this experiment was to determine whether, in xylene solution, the condensation between ethylic bromovalerate and ethylic methylmalonate might not proceed in a different manner from that in alcoholic solution, yielding derivatives of glutaric acid.

Fifteen grams of sodium in the form of powder* (molecular sodium) were suspended in about 400 c.c. of xylene and 117 grams of ethylic methylmalonate added; at the ordinary temperature the sodium dissolved only slowly, but, on slightly warming, a violent evolution of hydrogen took place, and the sodium derivative of ethylic methylmalonate separated as a pasty mass, in fact, the contents of the flask became so thick that more xylene had to be added. Ethylic α -bromisovalerate (141 grams) was then poured into the cooled solution, but no perceptible action occurred, although the sodium derivative dissolved in the mixture; the flask was therefore connected with a reflux condenser and heated to boiling on a sand bath for five hours, when sodium bromide separated in large quantities.

* As obtained by melting the sodium under the xylene in a corked flask and shaking vigorously.

When cold, the product was mixed with water, the xylene solution separated, and the aqueous liquid extracted three times with small quantities of xylene. The combined extracts were dried with calcium chloride, and the xylene distilled off as far as possible under the ordinary pressure; as soon, however, as the thermometer began to rise rapidly, the residue was transferred to a smaller flask, and the fractionation continued under diminished pressure (80 mm.); the chief fraction distilled at 200—210°, and weighed 71 grams, or 35 per cent. of the theoretical yield of pure ethylic salt.

Hydrolysis of the Ethylic Salt.—This ethereal salt was hydrolysed by means of a 50 per cent. solution of sulphuric acid in the manner described in the previous instance (p. 284); after 12 hours, all oil having disappeared, the product was distilled with steam.

The *sulphuric acid solution*, on cooling, deposited a large quantity of crystals, which melted indefinitely at 160—170°, but on twice recrystallising from water, the melting point rose to 174—175°, and remained constant. The following figures were obtained on analysis, showing that the substance was *trans-methylisopropylsuccinic acid*.

0.2102 gave 0.4327 CO₂ and 0.1512 H₂O. C = 54.97; H = 7.99.

C₈H₁₄O₄ requires C = 55.17; H = 8.04 per cent.

The filtrate from these crystals, on extraction with ether, &c., gave an oily residue, which, on standing, partially solidified; it was then spread on a porous plate, and the solid residue recrystallised from concentrated hydrochloric acid, when an acid was obtained melting sharply at 115—116°. This was evidently isopropylsuccinic acid,* since, on analysis, it yielded the following result.

0.2403 gave 0.4657 CO₂ and 0.1667 H₂O. C = 53.07; H = 7.70.

C₇H₁₂O₄ requires C = 52.52; H = 7.52 per cent.

The Steam Distillate.—As in the previous experiment (p. 285) this was made strongly alkaline with potash, evaporated to dryness, concentrated hydrochloric acid then added in large excess, and the whole extracted with ether; in this way, a solid substance was obtained which melted roughly at 110—120°, and on recrystallising four times from concentrated hydrochloric acid, gave *cis-methylisopropylsuccinic acid* melting constantly at 125—126°.

0.1926 gave 0.3905 CO₂ and 0.1388 H₂O. C = 55.29; H = 8.01.

C₈H₁₄O₄ requires C = 55.17; H = 8.04 per cent.

The quantities of these two acids melting at 126° and 175° respectively were about equal.

* The formation of this substance is obviously due to the presence of traces of ethylic malonate in the ethylic methylmalonate used.

Cis- and *trans*-methylisopropylsuccinic acids are therefore formed in about equal proportion by the action of ethylic α -bromisovalerate on the sodium compound of ethylic methylmalonate in xylene solution, whereas the same condensation conducted in alcoholic solution yields the *cis*-modification only.

XXVIII.—*Available Potash and Phosphoric acid in Soils.*

By T. B. WOOD, M.A., Secretary to Cambridge and Counties
Agricultural Education Scheme.

IN a paper by Dr. Bernard Dyer (Trans., 1894, 115—167) a convenient method is given for determining the available minerals in soils.

Dr. Dyer determined the sap-acidity of the smaller roots of a great number of plants, and found that on the average the sap-acidity might be taken as equivalent to that of a citric acid solution containing 1 per cent. of the crystallised acid. He then determined, in different samples of soil, the percentages of potash and phosphoric acid soluble in a citric acid solution of the strength above mentioned. The samples were taken from the various plots in the permanent barley field at Rothamsted, and the analyses, thus conducted, indicated very satisfactorily the relative amounts of available potash and phosphoric acid in each plot, as evidenced by the known yield and manuring.

A determination of the percentage of potash and phosphoric acid soluble in a 1 per cent. citric acid solution, would thus appear to give a trustworthy and rapid indication of the amount of available potash or phosphoric acid in any soil.

For the last four years, I have taken part in the management of the experimental plots of the Norfolk Chamber of Agriculture, and of the Suffolk County Councils, and during that time I have come across most striking variations in the effects of potash and phosphatic manures on the different soils.

It seemed to me that an examination of these soils by Dyer's method might give important evidence as to its technical usefulness.

The crops grown on the plots have included most of the ordinary agricultural crops, but for the purpose of this paper I quote only the results obtained with barley, in order that they may be more strictly comparable with those tabulated in Dr. Dyer's paper. The annexed table shows the average yield of several years' crops.

Table showing Yield of Barley in Bushels per Acre.

	Higham.	Warham.	Bramford.	Flitcham I.	Flitcham II.
No manure	25	29	38	—	—
Nitrate of sodium .. } Superphosphate.... } Potassium salts }	44	40	55	54	38
Superphosphate.... } Potassium salts }	30	33	37	—	—
Nitrate of sodium .. } Potassium salts }	38	37	52	—	—
Nitrate of sodium .. } Superphosphate.... }	41	37	51	9	16
Nitrate of sodium	40	37	51	—	21
Potassium salts	—	29	39	—	—

Quantities of Manures.

In each case the quantities used were as follows.

Superphosphate..... 3 cwt. per acre.

Potassium salts..... 1 cwt. per acre, as sulphate or chloride.

Nitrate of sodium 1 cwt., and in some cases 2 cwt. per acre.

Effect of Potash Manures.

From this point of view these soils may be divided into two groups.

I. Those to which the addition of potash produces only a small increase in the yield of corn—

Average.

Higham, Warham, Bramford $1\frac{1}{6}$ bushel per acre.

II. Those to which an equal addition of potash produces a very great increase in the yield of corn—

Flitcham I.

Flitcham II.

Average.

45 bushels

22 bushels

$33\frac{1}{2}$ bushels per acre.

The soils of Group I must evidently contain an abundance of readily available potash, whilst those of Group II must be deficient in this constituent in an available condition. Accordingly the soils of the first group should contain much potash soluble in 1 per cent.

citric acid, whilst those of the second group should contain but little potash soluble in that solvent.

I have obtained samples of all the soils through the kindness of members of the Norfolk Chamber and of the East and West Suffolk Technical Education Committees, to whom I now tender my best thanks.

The soils are all very similar, being light soils on chalk subsoil.

Analysis of the Soil.

The samples were air-dried, sifted, &c., and the moisture determined in the air-dried fine soil, which was then used for all the other determinations, the results being thus calculated on the dry soil. Nitrogen, organic matter, phosphoric acid, lime, potash soluble in hydrochloric acid were all determined by the ordinary methods; the hydrochloric acid used was a mixture of the strong acid with its own volume of water, 10 grams of the soil being boiled with 50 c.c. of the dilute acid for half an hour, evaporated nearly to dryness, and extracted with water. The potash soluble in 1 per cent. citric acid was determined exactly as directed in Dyer's paper.

The results are appended in the annexed tables.

	Higham.	Warham.	Bramford.	Flitcham I.	Flitcham II.
Moisture	7·5	0·87	1·8	1·6	1·9
Organic matter	4·63	1·97	2·51	5·5	4·12
Nitrogen	0·134	0·130	0·130	0·18	0·19
Phosphoric acid	0·218	0·11	0·23	0·20	0·15
Lime	5·88	0·76	1·96	17·1	5·6
Total potash	0·83	—	—	0·65	—
Potash soluble in HCl	0·171	0·185	0·180	0·14	0·135
Potash soluble in 1 per cent. citric acid	0·013	0·012	0·019	0·0063	0·0084

Table showing Increase produced by Soluble Potash Manure side by side with the amount of available Potash as shown by Solubility in 1 per cent. Citric acid.

	Increase bushels per acre.	Available potash by 1 per cent. citric acid.
Higham	$\frac{1}{2}$	0·013
Warham	1	0·012
Bramford	2	0·019
Average Group I	$1\frac{1}{6}$	0·0147
Flitcham I	45	0·0063
Flitcham II	22	0·0084
Average Group II	$33\frac{1}{2}$	0·00735

From the above table, it will be seen that Dyer's method shows twice as much available potash in the Group I soils as in the Group II, and this result agrees well with the results of the manurial experiments, which showed so clearly that Group I soils contained much more available potash than Group II.

The agreement would have been still more striking had not the occupier of the land at Flitcham applied two dressings of chloride of potassium, between the times when the field experiments were made there and the samples of soil were taken for analysis.

Dyer's method thus shows clearly the very different amounts of available potash in the two groups of soils; indeed, had it been applied to the Flitcham soils in the first instance, it would have indicated, more rapidly, and more economically than the field experiments did, the necessity of applying soluble potash manures in order to grow a profitable crop.

At the end of Dr. Dyer's paper, there is a suggestion that, in order to make the results strictly comparable for all soils, sufficient citric acid should be added to neutralise all the chalk in the soil and leave 1 per cent. over.

As several of the above soils contained large amounts of chalk, I acted on this suggestion, but found that, under these experimental conditions, the amount of potash dissolved was nearly equal in the case of each of the three soils tried. The numbers are annexed.

	Higham.	Flitcham I.	Flitcham II.
Potash soluble in 1 per cent. citric acid. . .	0·013	0·0063	0·0084
Potash soluble in 1 per cent. citric acid + enough to neutralise all the chalk	0·017	0·018	0·015

In adding the extra citric acid, the following method of procedure was adopted. The soil was put into a Winchester quart, with 1 per cent. acid, as detailed in Dr. Dyer's paper, and the amount of citric acid required to neutralise the chalk was weighed out and added at the rate of about 1 gram per hour, with frequent shaking.

When most of the extra acid had been added, the solution was titrated, and found to be nearly 1 per cent. in strength. It was then left until the sixth day and titrated again, and a further small amount of acid added to make the strength 1 per cent. On the seventh day, the liquid was separated, and the dissolved potash determined as before.

As will be seen by the above numbers, this method gave no indication of the much greater amount of available potash in the

Higham soil than in the two soils from Flitcham, and I venture to suggest that the clearest indication of the amount of available potash is obtained by extracting the soil with 1 per cent. citric acid, without regard to the amount of chalk contained in it.

It seems to me, also, that by doing so one is imitating more nearly the conditions under which the plant obtains its potash, for there is no evidence to show that the acidity of the root juice is greater when the soil is more calcareous.

Available Phosphoric acid.

Among the results of the Norfolk and Suffolk experiments are many numbers referring to the growth of swede turnips with different manures, and I have picked out the following as giving a graduated series in which the effect of superphosphate is practically nil, very great, and intermediate between these two.

	Bramford.		Higham.		Warham.	
	Tons.	Cwt.	Tons.	Cwt.	Tons.	Cwt.
No manure.....	8	7	4	5	4	18
Superphosphate, 4 cwt...	8	9	6	15	8	13
Nitrate of soda, 2 cwt. ..	10	11	—	—	—	—
Nitrate of soda, 2 cwt. } Superphosphate, 4 cwt. }	11	9	7	3	—	—

It will be seen that the effect of superphosphate is practically nil at Bramford, while at Higham it is considerable, and at Warham greater still.

I have estimated the phosphoric acid in these three soils by Dyer's method, both with and without the addition of extra citric acid to neutralise the chalk, the extra acid being added in the manner described above. The results are given in the following table.

	Bramford.	Higham.	Warham.
Lime (CaO)	1·96	8·88	0·76
Phosphoric acid (P ₂ O ₅) I.....	0·23	0·218	0·11
" " II.....	0·080	0·012	0·0076
" " III.....	0·085	0·056	—

I being phosphoric acid soluble in strong nitric acid on boiling ;

II, phosphoric acid soluble in 1 per cent. citric acid; III, phosphoric acid soluble in 1 per cent. citric acid using extra acid to neutralise the chalk.

The analytical numbers obtained with the 1 per cent. acid show very clearly the much greater amount of available phosphoric acid in the Bramford soil than in either of the others, and the much smaller and more nearly equal amounts in the soils from Higham and Warham. This agrees perfectly with the results obtained in the field experiments with swedes quoted above, and the method appears to give even better results for phosphoric acid than it did with potash.

When the extra citric acid was added, in the case of the Bramford soil with only 1.97 per cent. of lime, a slightly greater amount of phosphoric acid was dissolved; in the Higham soil, containing 5.88 per cent. lime, nearly five times as much P_2O_5 was dissolved as with 1 per cent. acid only. The Warham soil contained so little lime that no determination with extra acid was thought necessary.

Comparing the results obtained with and without the extra acid, it appears that the 1 per cent. acid only, the chalk being neglected, gives numbers more nearly proportional to those ascertained by field experiment; and again I think that this is only to be expected, for thus we imitate most nearly the solvent action of the plant juices.

In the case of the 1 per cent. acid and a soil rich in chalk, the large amount of carbonic acid evolved must have an appreciable solvent action on the potash and phosphates present. 100 grams of the Higham soil suspended in 1 litre of water through which purified carbonic anhydride was passed for 48 hours yielded the following numbers.

K ₂ O dissolved by water saturated with CO ₂	0·008 per cent.
P ₂ O ₅ " " 	0·011 "
K ₂ O soluble in 1 per cent. citric acid 	0·013 "
P ₂ O ₅ " " 	0·012 "

My thanks are due to Dr. T. H. Easterfield for many valuable suggestions given in the course of the work.

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XXX.—*The Production of Naphthalene and of Isoquinoline Derivatives from Dehydracetic acid.*

By J. NORMAN COLLIE, Ph.D., F.R.S.E., and N. T. M. WILSMORE, M.Sc. (Melbourne).

In a former paper by one of us (Trans., 1893, **63**, 329 *et seq.*), it was shown that under certain conditions diacetylacetone condenses with loss of water, forming a yellow, crystalline compound, melting at 108—109°, and this compound condenses further to a second yellow substance, which melts at 183—184°, and proved to be a naphthalene derivative. All the work then done with this second substance indicated, with considerable probability, that its constitution was 3 : 3'-dimethyl-2-acetyl-1 : 1'-dihydroxynaphthalene.

The present communication is an account of further research on these compounds, in which it was sought to elucidate the mechanism of the reactions taking place in their formation, and to obtain further evidence as to their constitution.

It would appear from what follows that, of the possible tautomeric forms of diacetylacetone, one is comparatively stable and incapable of condensation to the above compound, whilst another is unstable—readily changing into the stable form, or condensing by union of 2 mols. with loss of water. It is interesting to note in this connection that W. H. Perkin (Trans., 1892, **61**, 827) has shown, from the magnetic rotation, that at a temperature of 60·4°, two double linkings are present in the diacetylacetone molecule, whilst at lower temperatures, it tends to pass into the trihydroxy-derivative.

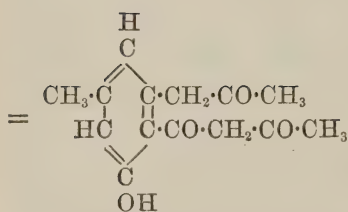
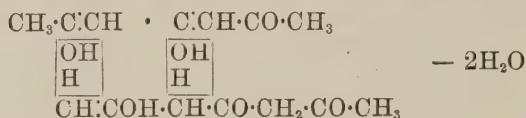
The condensation occurs most readily when the diacetylacetone—which acts as a dibasic acid to strong bases—is combined with only half its equivalent of barium. Possibly 2 mols. are here united by an atom of barium in the form of an acid salt, this being a first step to the more complete union. Certainly a univalent metal, such as sodium or potassium, cannot be substituted for barium; but, on the other hand, the formation of the yellow substance will take place, even if the whole of the barium be removed as carbonate by a current of carbonic anhydride. In all other cases, the barium hydroxide liberated by the condensation hydrolyses some of the remaining diacetylacetone, forming barium acetate. The condensation is, however, not complete in any case; and at most, only half of the theoretical yield has been obtained.

In accordance with the foregoing, we would suggest that the normal barium salt of diacetylacetone should also be written double,

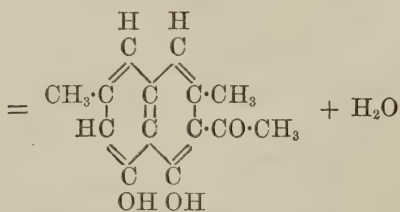
having the constitution $\text{Ba} < \begin{smallmatrix} \text{O} \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C} \cdot (\text{CH}_3) \text{O} \\ \text{O} \cdot \text{C}(\text{CH}_3) : \text{CH} \cdot \text{CO} \cdot \text{CH} : \text{C} \cdot (\text{CH}_3) \text{O} \end{smallmatrix} > \text{Ba}$, instead of that suggested by Feist (*Annalen*, 1890, **257**, 276).

Owing to the difficulty with which the yellow compounds react, comparatively little progress has been made with them. From the second, dimethylacetyldihydroxynaphthalene—a dimethylnaphthalene has been prepared, which, on oxidation, yields 1 : 3 : 4-methylphthalic acid. Also, by the action of strong sulphuric acid, the acetyl group appears to have been removed, leaving a colourless substance.

Very little direct experimental evidence as to the constitution of the first substance, m. p. 108—109°, has been obtained. In all probability, it is a benzenoid compound, having long side-chains which unite to form dimethylacetyldihydroxynaphthalene. The condensation of diacetylacetone, therefore, takes place in two stages.

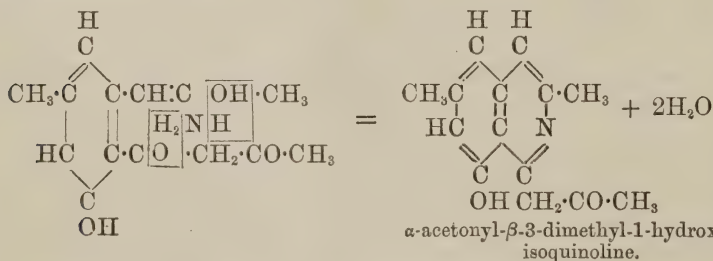


First yellow compound.

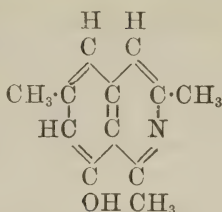


Dimethylacetyldihydroxynaphthalene.

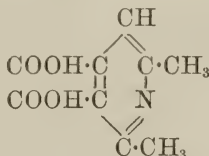
The probability of the benzenoid character of the first compound is heightened by its peculiar behaviour with ammonia, resulting in the formation of what appears to be a derivative of isoquinoline. The reaction seems to be

 α -acetyl- β -3-dimethyl-1-hydroxy-isoquinoline.

By heating this new base with strong sulphuric acid, part of the side-chain is removed, leaving $\alpha\alpha'$ -3-trimethyl-1-hydroxyisoquinoline (1' : 3' : 3-trimethyl-1-hydroxyisoquinoline),

*αα'-3-trimethyl-1-hydroxy-isoquinoline.*

This second base, on oxidation, gives a pyridinecarboxylic acid, which is probably *αα'*-dimethylpyridine- $\beta\gamma$ -dicarboxylic acid (2 : 6-dimethylpyridine-4 : 5-dicarboxylic acid),



Hence one more example is to hand of the generalisation emphasised in the former communication above referred to, respecting the tendency of the aldehydic and ketonic derivatives to produce complex compounds by reactions similar to those occurring in nature.

Condensation of Diacetylacetone.

The immediate starting point in most of these experiments was the yellow barium salt of diacetylacetone, first described by Feist (*Annalen*, 1890, **257**, 276). This was prepared from dehydracetic acid by boiling it with strong hydrochloric acid until the evolution of carbonic anhydride ceased, and then evaporating the solution to dryness in a vacuum; the compound, $\text{C}_7\text{H}_{11}\text{O}_3\text{Cl}$, thus obtained (*Trans.*, 1891, **59**, 619) was dissolved in water, and the strongly acid solution neutralised with solid sodium carbonate to produce a solution of dimethylpyrone. It was found convenient to dilute this so that 4 c.c. corresponded with 1 gram of the dehydracetic acid taken. On heating to boiling and adding excess of hot, strong solution of barium hydroxide (2.4 grams of barium hydroxide to 1 gram of the original dehydracetic acid), the sparingly soluble barium salt of diacetylacetone was precipitated. This was washed rapidly with hot water on the filter pump, and used as soon as cold. The weight of barium salt, dried on the pump, was about equal to the weight of barium hydroxide taken. A sample of the salt, free from barium carbonate, washed with hot water, and then with alcohol and ether, and dried in a vacuum over sulphuric acid, was found to contain 49.32 per cent. of barium, which agrees with Feist's determination. $\text{Ba}_2(\text{C}_7\text{H}_5\text{O}_5)_2$ requires 49.46 per cent.

The moist salt has a strongly alkaline reaction, readily absorbing carbonic anhydride from the air, and turning reddish, dimethylpyrone and other products being formed.

The original method of bringing about the condensation was as follows. The barium salt, made into a thin paste with water, was nearly dissolved in hydrochloric acid of about 15 per cent., leaving the solution faintly alkaline, and the solution was filtered from traces of barium carbonate, &c.; on standing, the *first yellow compound*, melting at 108—109°, crystallised out, and on concentrating the mother liquor under diminished pressure, a further crop of crystals was obtained, consisting, however, of the *second substance*—*dimethylacetyldihydroxynaphthalene*. The residue obtained on evaporation to dryness contained barium chloride and acetate (the latter apparently formed by hydrolysis of some of the diacetylacetone), mixed with a considerable quantity of resinous matter. The distillate contained, among other things, acetylacetone. The barium salt dissolved, and the solution became neutral when hydrochloric acid equivalent only to half the barium present had been added. If acid stronger than that mentioned were used, there was a tendency for free diacetylacetone to be formed. The yield of the yellow substances averaged about 22 per cent. of the weight of dehydracetic acid taken.

Several modifications of this method were tried.

I. The solution of dimethylpyrone was divided into two equal parts. One part was converted into barium salt, and this was then mixed with the other part, in which it dissolved. A very poor yield was obtained, owing, probably, to the solution being too alkaline from the excess of barium hydrate, which cannot be completely washed out of a large precipitate of the barium salt of diacetylacetone without serious loss of the latter.

II. Acetic acid was substituted for hydrochloric acid as a solvent for the barium salt. The latter substance, from 4.5 grams of dehydracetic acid, was treated with 16 c.c. of acetic acid of sp. gr. 1.05, which neutralised it. Diacetylacetone was the only product. In another case, however, where acetic acid equivalent to the barium was added, diacetylacetone was again precipitated; but the filtrate, on standing, deposited considerable quantities of the first yellow substance. By using only half the amount of acetic acid necessary to neutralise the barium, the reaction went as with hydrochloric acid. In one case, from 12.5 grams of dehydracetic acid, 2.4 grams of the first yellow compound were obtained, or about 19 per cent. In another, from 4.5 grams of dehydracetic acid, using 20 per cent. acetic acid for neutralising, 2 grams of the yellow substance were obtained, or 44 per cent. In this case, the solution of the barium salt in acetic acid was warmed, and dimethylacetyldihydroxynaph-

thalene was the chief product. The method with acetic acid appeared too uncertain in its results to warrant an experiment on a larger scale.

III. The barium salt, from 4.5 grams of dehydracetic acid, was suspended in water, and the barium was neutralised with a current of carbonic acid. The barium carbonate was filtered off, and the solution evaporated rapidly under diminished pressure to 30 c.c. 1.5 grams of the first yellow compound, in a pure condition, crystallised out, being a yield of 33 per cent. The distillate contained diacetylacetone. The solution was free from barium, so that diacetylacetone, in an unstable, tautomeric form, that is, in a nascent state, must have been present. The method is, therefore, of interest, but is inconvenient owing to the large bulk of solution which has to be evaporated. This means serious loss by hydrolysis of the diacetylacetone to acetylacetone, acetic acid, &c., together with resinous substances, when dealing with any but small quantities.

IV. A modification, which gave fairly good results, even on a pretty large scale, consisted mainly in the use of oxalic acid for neutralising the barium salt. A 20 per cent. solution of (crystalline) oxalic acid, warm enough to keep the acid dissolved, was used.

The mixture became neutral when oxalic acid, equivalent to half the barium present, had been added. The barium oxalate was filtered off rapidly, preferably first with linen, and the filtrate allowed to stand over night, when very pure crystals of the first yellow substance were obtained. It was found better not to concentrate the filtrate from these, but to precipitate again with barium hydrate, and treat the barium salt of diacetylacetone thus recovered with oxalic acid as above, when a further, though much smaller, quantity of the yellow substance could be obtained. It did not appear to signify if oxalic acid were added until the reaction was acid. In one case, from 200 grams of dehydracetic acid, 63 grams of the pure first yellow compound was obtained, being a yield of 31.5 per cent. The latter yield was probably due to the smaller amount of mineral salt left in solution.

V. The barium salt of diacetylacetone, from nearly 3 grams of dehydracetic acid, was treated with a dilute alcoholic solution of diacetylacetone; when about 4 grams of the latter had been added, the barium salt had entirely disappeared. On filtering to remove traces of barium carbonate, and concentrating to 30 c.c., no precipitate was formed; but, on standing for several days, about 1 gram of the first yellow substance was deposited. The filtrate from this was made alkaline with ammonium carbonate, and filtered; on evaporation, a semi-crystalline mass was left, which yielded a further small quantity.

VI. An experiment with diacetylacetone alone was next tried. The barium salt, from 50 grams of dehydracetic acid, was treated with excess of hydrochloric acid, and the diacetylacetone formed extracted with chloroform; on evaporating the latter, 33 grams of diacetylacetone were left. This was heated for several days at 100° in a sealed tube; water gradually separated, and the whole finally set to a mass of crystals of dimethylpyrone, no yellow compound being formed.

Experiments V and VI seem to lend further support to the hypothesis that the formation of an acid barium salt of diacetylacetone, or of the latter substance in a "nascent" state, are important steps towards the condensation.

VII. Dimethylpyrone was treated with strong potash, and the potassium salt which separated was collected; on adding hydrochloric acid until the reaction was only faintly alkaline, the salt dissolved, but no yellow coloration appeared on standing. Ultimately, a white, crystalline precipitate of dimethylpyrone was thrown down.

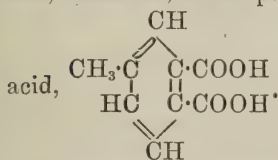
The theoretical yield from dehydracetic acid, supposing all the diacetylacetone to condense, would be 73.8 per cent. of the first yellow compound, or 68.5 per cent. of dimethylacetyldihydroxynaphthalene. Hence in all the methods tried, there was serious loss, which occurred almost entirely in the process of condensation of the diacetylacetone, since the preliminary reactions were nearly quantitative.

Dimethylacetyldihydroxynaphthalene.

It was mentioned in the former paper that, by distilling the diacetate over heated zinc dust, a naphthalene hydrocarbon, melting at $92-93^{\circ}$, was obtained, which appeared to be 2 : 3 : 3-trimethylnaphthalene. This experiment was repeated, as it seemed somewhat curious that a trimethyl derivative should be formed. 50 grams of the diacetate were decomposed by zinc dust at the lowest temperature which would give the naphthalene hydrocarbon; but only a very small yield, in all less than 2 grams of the hydrocarbon, was obtained. This was purified by sublimation between watch glasses, and was finally found to melt at $67-69^{\circ}$; it could also be sublimed at the same temperature. On analysis, numbers which agreed with those required by a dimethylnaphthalene, were obtained.

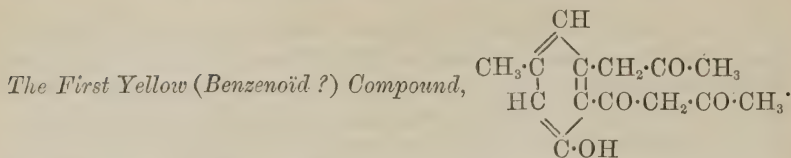
	Found.	Calculated for $C_{10}H_6(CH_3)_2$.
C.....	91.4	91.3
H.....	8.7	8.7

It was hardly attacked by boiling with chromic acid; but, by heating under pressure, or boiling with dilute nitric acid for a long time, it ultimately yielded an acid as a flocculent precipitate. This acid was soluble in water, but was removed from its aqueous solution by agitation with ether. On heating alone, it yielded a crystalline sublimate, and it gave the fluorescein reaction. The melting point of a few crystals was somewhere about $115-120^{\circ}$ (?), whilst Young (*Ber.*, 1892, 25, 2108) gives for 1 : 3 : 4-methylbenzenedicarboxylic acid the melting point 124° . The silver salt, on analysis, gave 55.5 per cent. of silver. $C_9H_6O_4Ag_2$ requires $Ag = 54.8$. The acid was, therefore, in all probability 1 : 3 : 4-methylbenzenedicarboxylic



The action of strong sulphuric acid on dimethylacetyldihydroxynaphthalene was studied with a view of removing the side-chains. On dissolving 7 grams of the substance in about 30 c.c. of 98 per cent. sulphuric acid, a solution was obtained exactly the colour of chromic acid; but, on warming to $60-80^{\circ}$, the colour disappeared; it was now poured into water, when a white emulsion was formed, which finally changed to a granular mass of crystals. These were dissolved in cold alcohol, and boiled with animal charcoal; on adding water, an oil was precipitated, which crystallised on standing. By again dissolving in alcohol and precipitating with water, a white, crystalline precipitate was obtained, which was dried over sulphuric acid and analysed. The results were, however, unsatisfactory, Found, $C = 74.3$; $H = 6.8$. $C_{12}H_{12}O_2$ requires $C = 76.6$; $H = 6.3$. The crystals had a very low melting point; they were soluble in cold soda, but reprecipitated by acids. With chlorine or bromine water, they gave a brilliant purple coloration, but there was no reaction with ferric chloride. On warming with sulphuric acid, violet vapours were given off, but on adding water to the solution, nothing but a black residue, was obtained.

On fusion with potash, dimethylacetyldihydroxynaphthalene yielded only a charred mass. With fuming nitric acid, a nitro-compound may have been formed, but in quantity too small for investigation. The action of hydroxylamine and of aniline was again tried, but the results were as described in the last paper. With ammonia, nothing but a tarry mass was produced.



Owing to the great readiness with which this substance changes into dimethylacetyldihydroxynaphthalene, very little could be done with it; this occurs even if its solution in strong or aqueous alcohol is boiled for some time, or concentrated. In the latter case, the change usually takes place suddenly, the less soluble product crystallising out. With hydroxylamine, however, it forms a dioxime.

Nitrogen found, 9.9. $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4$ requires 10.0.

It is soluble in alkalis, more easily in potash than in soda; and if the solution is acidified at once, the original substance is reprecipitated, but if the alkaline solution is allowed to stand, or is warmed, the corresponding salt of dimethylacetyldihydroxynaphthalene is formed, the solution changing colour from lemon-yellow to deep orange. Hence salts of the first compound could not be isolated.

With ammonia, the action was different; the compound dissolved easily in aqueous ammonia, and, on evaporation over sulphuric acid in a vacuum, a yellow substance was left, easily soluble in alcohol and, to some extent, in water, giving intensely yellow solutions, which were neutral to litmus. In one preparation, an attempt was made to boil off the excess of ammonia, but decomposition ensued, a strong smell of pyridine bases being apparent. On adding hydrochloric acid to the solutions of the new substance, no precipitate was formed; but, in the case of the aqueous solution, the colour disappeared almost entirely. On evaporating its solutions, the substance crystallised out in minute, yellow needles, which contained nitrogen. It was soluble in warm, dilute soda solution, but insoluble in strong, although it decomposed to some extent. In neither case, however, was ammonia evolved. In some cases, the solution of the benzenoid compound in ammonia deposited the new substance on merely standing, indicating that probably an ammonium salt of the former was first formed.

The new compound is believed to be a derivative of isoquinoline. It crystallises with $\frac{1}{3}$ mol. of water, which it retains on drying over sulphuric acid, but loses at 130° , leaving a yellow, amorphous powder.

0.2937 gave 0.7679 CO_2 and 0.1733 H_2O . C = 71.31; H = 6.56.

0.3152 „ 0.8251 „ 0.1921 „ C = 71.39; H = 6.77.

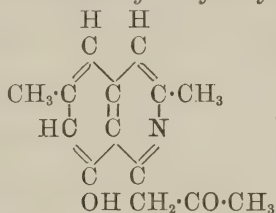
0.2507 „ 13.3 c.c. moist nitrogen at 19° and 766 mm. N = 6.00.

0.7778 lost 0.0193 H_2O at 130° . H_2O = 2.48.

$\text{C}_{14}\text{H}_{15}\text{NO}_2 \cdot \frac{1}{3}\text{H}_2\text{O}$ requires C = 71.49; H = 6.64; N = 5.96; H_2O = 2.55 per cent.

The molecular weight of the crystallised base was taken by Raoult's method, using glacial acetic acid as the solvent. A mean of two determinations gave the molecular weight 203, or, allowing for the water of crystallisation, 272. Calculated, for the anhydrous base, $C_{14}H_{15}NO_2$, 229, or for the crystalline substance, 235.

α-Acetonyl-α' : 3-dimethyl-1-hydroxyisoquinoline,



The base, when pure, crystallises from alcohol in bright yellow, minute, silky needles, melting at $164-165^\circ$ (uncorr.). It is easily soluble in alcohol or acetic acid, but only sparingly in water; these solutions are deep yellow. The free base oxidises readily in solution, particularly in presence of alkalis and on warming; hence in its preparation the temperature must be kept low, and the ammonia evaporated in a vacuum. It dissolves readily in dilute acids, yielding a nearly colourless solution, from which the corresponding salts may be crystallised. The hydrochloride crystallises from dilute hydrochloric acid in beautiful, pale yellow needles, melting at about 242° with decomposition; it is slightly hydrolysed in dilute aqueous solution, the latter becoming yellow. The reaction of the aqueous solution is therefore acid.

0.1177 gave 0.0656 AgCl. Cl = 13.76.

0.101 „ 5.2 c.c. moist nitrogen at 21° and 750 mm. N = 5.7.

$C_{14}H_{15}NO_2Cl$ requires Cl = 13.34; N = 5.3 per cent.

With platinic chloride, a brownish-yellow platinochloride is precipitated as an amorphous (?) powder. On heating, a strong smell of quinoline was evolved, and oily drops formed on the lid of the crucible.

0.2198 of the dry salt gave 0.0495 Pt. Pt = 22.52.

$(C_{14}H_{15}NO_2)_2 \cdot H_2PtCl_6$ requires Pt = 22.55 per cent.

The base is not acted on by phosphorus trichloride, and with the pentachloride it merely chars. It decomposes on heating with acetic anhydride, but no acetate could be isolated. It does not appear to form an oxime when treated with hydroxylamine, although it seems to give a crystalline, but very unstable, compound with sodium hydrogen sulphite. On distilling over zinc dust, neither pyridine nor quinoline derivatives could be detected.

On oxidation with potassium permanganate, an acid was obtained in very small quantity as an amorphous powder, sparingly soluble in water; this acid formed an insoluble lead salt, but could not be purified. By heating with solid soda or with zinc dust, a substance, resembling lutidine, was given off, and condensed as oily drops, which fumed when brought near strong hydrochloric acid, and gave a crystalline platinochloride on treatment with platinic chloride.

On warming with strong sulphuric acid, the acetyl-derivative described in the last section, part of the side chain appeared to be removed, leaving a methyl group; 10 grams of the base were treated with 30 grams of strong sulphuric acid, which dissolved it, forming an intensely yellow solution; on warming to 60–80°, acetic acid was given off, and the solution became darker, but had far less colouring power. The whole was then poured into about 300 c.c. of water, and, on standing, a nearly white, amorphous substance separated, which was filtered off; the filtrate contained acetic acid, but no trace of an ammonium salt. When the precipitate, which was nearly insoluble in water or alcohol, was warmed with barium carbonate made into a paste with water, a second base was liberated, and could be extracted with alcohol; it did not contain sulphur. After being recrystallised five times from alcohol, it began to blacken slightly at 225°, and melted at 247–280° (uncorr.).

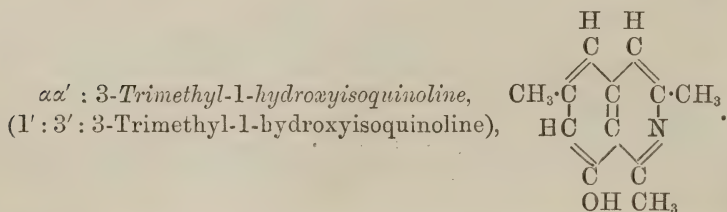
0.1225 gave 0.346 CO₂ and 0.0813 H₂O. C = 77.03, H = 7.37.

0.2673 „ 0.7558 CO₂ and 0.174 H₂O. C = 77.12, H = 7.23.

0.2838 „ 18.8 c.c. moist nitrogen at 18.5° and 755 mm. N = 7.74.

0.2503 „ 16.4 c.c. N at 19° and 765.5 mm. N = 7.57.

C₁₂H₁₃NO requires C = 77.00; H = 6.95, N = 7.49 per cent.



α' : 3-Trimethyl-1-hydroxyisoquinoline crystallises from alcohol in minute, lemon-yellow needles, but much less readily than the first base; and the colour, whether in the solid state or in solution, is far less intense than that of the latter. It dissolves to some extent in water, yielding a yellow solution with neutral reaction. The salts are amorphous or very difficult to crystallise, and are colourless, or nearly so; they are slightly hydrolysed by water, and have, consequently, an acid reaction. The hydrochloride, when pure, is colourless. It crystallises with difficulty from dilute alcohol, and contains

water of crystallisation; it does not appear to form a platinumchloride. Owing to lack of material, an estimation of chlorine alone could be made.

The base is not acted on by phosphorus trichloride, and chars on heating with the pentachloride. On heating with excess of acetic anhydride at 150—160° in a sealed tube it appeared merely to dissolve, for the unchanged base was recovered on evaporating the anhydride. A very small amount of a white substance was, however, formed, which may have been an acetate, but was insoluble in all the usual solvents. It did not appear to be crystalline, and on heating it charred without melting.

The base does not give off pyridine or quinoline derivatives when distilled over heated zinc dust, or when heated with solid soda.

During one preparation of this substance, a bright yellow powder was left on dissolving the crude product in alcohol, and, as it contained sulphur and nitrogen, was probably a sulphonic acid; the amount, however, was too small for analysis. This substance charred at 270—280° without melting. It was nearly insoluble in water or alcohol, but dissolved in alkalis, forming a colourless solution which became brilliantly yellow on exactly neutralising with acids, although the colour of this yellow powder was again discharged by a slight excess of the latter.

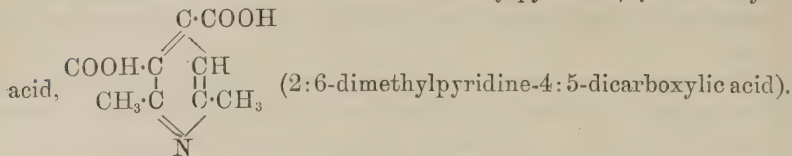
On oxidising the trimethylhydroxyisoquinoline with potassium permanganate, an acid was obtained which, on distilling with solid soda, gave off a substance resembling lutidine, but in quantities too small for investigation. This acid was soluble with difficulty in water, but could not be crystallised from that solvent, and it was insoluble in all the other usual solvents. The ammonium salt, however, was very soluble in water, and crystallised on evaporation in a vacuum over sulphuric acid; but, unfortunately, it contained water of crystallisation which could not be driven off without loss of ammonia, and it, therefore, could not be analysed.

An attempt was made to purify the acid as follows. It was precipitated as the lead salt, and the precipitate was warmed with acetic acid, which left any oxalate undissolved; the filtrate was then boiled several times with sugar charcoal (animal charcoal was found to remove the acid itself), and the acid again precipitated as lead salt, which was decomposed with sulphuretted hydrogen. On evaporating the filtrate from the lead sulphide, the acid was left as a white powder which decomposed at about 250° without melting. An analysis was made, but was not satisfactory.

0.091 gave 0.180 CO₂ and 0.0451 gram H₂O. C = 53.96, H = 5.51.
0.13 „ 8.4 c.c. moist nitrogen at 20° and 754 mm. N = 7.32.

C₉H₉NO₄ requires C = 55.39; H = 4.62; N = 7.18 per cent.

The acid is believed to be $\alpha\alpha'$ -dimethylpyridine- $\beta\gamma$ -dicarboxylic

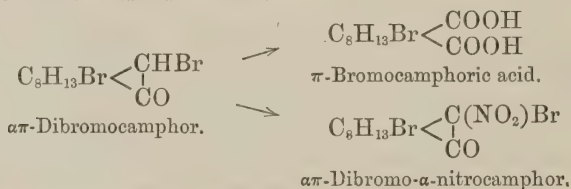


The inability to obtain it pure and in quantity is the more to be regretted, as it is the only one of the possible lutidinedicarboxylic acids hitherto unprepared.

XXXI.—Isomeric π -Bromo- α -nitrocamphors.

By ARTHUR LAPWORTH, D.Sc., and FREDERIC STANLEY KIPPING, Ph.D., D.Sc.

THE $\alpha\pi$ -dibromocamphor obtained by heating α -bromocamphorsulphonic bromide (Kipping and Pope, Trans., 1895, **67**, 371), is oxidised by boiling nitric acid, giving π -bromocamphoric acid, but at the same time a large proportion of the compound is converted into a dibromonitrocamphor which resists oxidation.

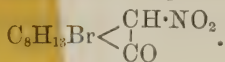


The study of π -bromocamphoric acid and of the numerous compounds derived from it (Kipping, Proc., 1895, 33, 88, 210) is not yet finished, but the investigation of the nitro-compound has been brought to a conclusion, and the results are recorded in this paper.

$\alpha\pi$ -Dibromo- α -nitrocamphor is a colourless, crystalline substance, insoluble in alkalis; the last fact points to the conclusion that the nitro-group and the bromine atom are both united with one and the same carbon atom as shown in the above formula; consequently the formation of this nitro-compound is analogous to that of $\alpha\alpha$ -nitrobromocamphor from ordinary α -bromocamphor.

When $\alpha\pi$ -dibromo- α -nitrocamphor is heated with alcoholic potash it undergoes reduction, and the potassium derivative of π -bromo- α -nitrocamphor is formed. The π -bromo- α -nitrocamphor, prepared from this product, is insoluble in water, but it dissolves readily in alkalis, and has altogether a pronounced acid character, yielding a series of well-defined, metallic derivatives; for these reasons, and

also because it gives π -bromocamphoric acid on oxidation, it must be regarded as having the constitution represented by the formula

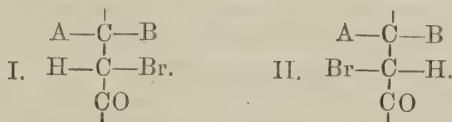


π -Bromo- α -nitrocamphor is a very interesting substance from a crystallographic point of view, inasmuch as it is trimorphous, and the three different forms are all obtainable by crystallisation from solvents at ordinary temperatures, two of them in a condition suitable for goniometrical measurement. It is also interesting chemically because of the readiness with which it is converted into a well-defined, crystalline isomeride when its solution in concentrated hydrochloric acid is boiled during a short time.

This isomeride, like the original bromonitrocamphor, has a distinctly acid character, and forms a series of metallic derivatives; like the original bromonitrocamphor, moreover, it is converted into π -bromocamphoric acid on oxidation. There is, on the other hand, such a considerable difference between these two compounds in other respects, that they must be regarded as chemically, and not merely physically, distinct; on reduction, for example, they yield isomeric, but not identical, bromamidocamphors.

On first attempting to account for the existence of the two bromo-nitro-compounds in question, on the basis of the facts mentioned above, it seemed probable that their isomerism might be due to a difference in configuration; that is to say, that they might be regarded as comparable to the ordinary *cis*- and *trans*-modifications of certain cycloïd compounds.

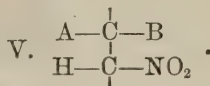
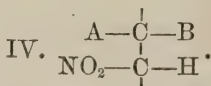
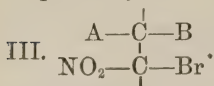
Whatever constitutional formula be finally adopted for camphor, it is highly improbable that the two hydrogen atoms of the $-\text{CH}_2\cdot\text{CO}$ group are similarly situated with respect to the rest of the atoms in the molecule; consequently, when camphor is converted into α -bromocamphor by direct treatment with bromine alone, the halogen atom takes the place of a hydrogen atom in one position only, and the product contains a group of atoms which may be represented by *one* only of the following configurations.



If, now, this bromocamphor is converted into a nitro-derivative by the displacement of the remaining hydrogen atom of the original $-\text{CH}_2\cdot\text{CO}$ group, the position taken up by the nitro-group is determined by the previous introduction of the bromine atom.

Suppose, therefore, that I indicates the configuration of this

particular complex in α -bromocamphor, then $\alpha\pi$ -dibromo- α -nitrocamphor and the π -bromo- α -nitrocamphor formed from the latter, on treatment with alcoholic potash, may be represented by III and IV respectively.



But the nitro-group in π -bromo- α -nitrocamphor IV thus indirectly prepared may not be in the most favourable or stable position—this having been previously occupied by the α -bromine atom—and, on boiling with hydrochloric acid, isomeric change may occur (as it is known to do in so many cases under these conditions), the relatively more stable π -bromo- α -nitrocamphor of configuration V being formed.

This assumption, namely, that the α -substitution products of camphor may exist in stereochemically different forms is by no means novel, and has been made use of by Marsh (*Trans.*, 1890, **57**, 828) in order to account for the existence of iso-monobromocamphor; its general applicability in the case of the α -mono- and some of the $\alpha\alpha$ -di-substitution products is also obvious.

Notwithstanding the fact that in the present instance there are particularly strong grounds for adopting this view of the relation between the two compounds in question, the literature of camphor contains cases of isomerism, apparently of a similar kind, but which have been explained in quite a different manner. During recent years, Cazeneuve has described *three* isomeric α -nitro-derivatives of camphor; two of these were obtained by reducing a mixture of two isomeric chloronitrocamphors with the aid of the zinc-copper couple (*Bull. Soc. Chim.*, 1887, **47**, 920); one of them, α -nitrocamphor or " α -nitrocamphoric acid," melted at 100–101°; the other, $\alpha\beta$ -nitrocamphor, or " β -nitrocamphoric acid," was described as a camphor-like substance melting at 97–98°. The two compounds differed in specific rotatory power, and that of lower melting point was considered to be identical with, but a purer preparation of, Schiff's nitrocamphor (m. p. 83°). Cazeneuve did not attempt to account for the existence of these isomerides, and in his paper there are no facts which would discredit the assumption that the two substances are the *cis*- and *trans*-modifications respectively.

In later communications (*Bull. Soc. Chim.*, 1889, 243, 417, and 467), a third isomeride is described under the name of "camphonitrophenol." This α -nitrocamphor, obtained by boiling the isomeride, melting at 100–101°, with concentrated hydrochloric acid, crystallised from water with 1H₂O, became anhydrous when kept over sulphuric acid under reduced pressure, and then melted at 220°. Like the two isomerides previously described, this "camphonitro-

phenol" had a marked acid character, and decomposed metallic carbonates, yielding crystalline salts.

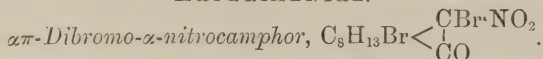
As a full discussion of this work would occupy too much space, it may be briefly stated that Cazeneuve assigned to "camphonitrophenol" the constitutional formula $C_8H_{14} < \begin{smallmatrix} C \cdot NO_2 \\ | \\ C \cdot OH \end{smallmatrix}$, and accounted for its formation from α -nitrocamphor by supposing that the latter first combined with the elements of hydrogen chloride, yielding the intermediate product, $C_8H_{14} < \begin{smallmatrix} CH \cdot NO_2 \\ | \\ CCl \cdot OH \end{smallmatrix}$, which then lost these two elements, but not the identical hydrogen atom which had just been added. In support of the formula given above, Cazeneuve showed that "camphonitrophenol" yielded an acetyl derivative on treatment with acetyl chloride, and he also prepared a number of other derivatives of a similar kind.

Now, the formation of an acetyl derivative from "camphonitrophenol" and by inference—since it does not appear to be expressly stated—the non-formation of such a compound from the isomeric α -nitrocamphor, is very important on account of its bearing on the relation between the two compounds; it was evidently desirable, therefore, to study the behaviour of the two π -bromo- α -nitrocamphors in this respect. Experiments which were made with this object brought out the fact, that the compound obtained directly from $\alpha\pi$ -dibromo- α -nitrocamphor was unchanged, even after prolonged boiling with acetyl chloride or acetic anhydride, whereas the isomeric π -compound, produced under conditions similar to those employed by Cazeneuve in preparing "camphonitrophenol," was readily converted into a crystalline acetyl derivative. The relation between the two π -bromo- α -nitrocamphors is, therefore, in all probability, analogous to that existing between α -nitrocamphor and "camphonitrophenol."

Even granting this to be true, the problem whether these compounds are structural or stereochemical isomerides can hardly yet be regarded as settled. On the one hand, the difference in chemical behaviour, which has just been mentioned, is not easily reconciled with the assumption that the substances are merely different in configuration; on the other, the constitutional formula assigned to "camphonitrophenol" by Cazeneuve is not, in the authors' opinion, quite free from objection. Other explanations might be suggested, the foregoing by no means exhausting the various possibilities, but, inasmuch as experimental evidence cannot be brought forward to support them, it is premature to adopt any particular view until this has been done.

It is proposed, therefore, to use the name π -bromo- α -isonitrocampa-phor for the isomeric substance obtained from π -bromo- α -nitrocampa-phor by the action of hydrochloric acid, and analogous to Cazeneuve's camphonitrophenol, in order to avoid the implication that it is analo-gous in constitution to the true nitrophenols.

EXPERIMENTAL.



Action of Nitric acid on π -Dibromocampa-phor.—Forty grams of π -di-bromocampa-phor are placed in a flask fitted with a reflux condenser, covered with a mixture of 300 grams of nitric acid (sp. gr. = 1.42) and 90 c.c. of water, and heated on the sand bath, a small quantity of acetic acid being added, in order to bring all the solid into solution by the time the liquid boils. Oxidation proceeds rapidly, nitrous fumes and bromine being copiously evolved, and after the action has gone on for about three hours, the solution is allowed to cool, when the liquid becomes cloudy, owing to the deposition of oily substances, but a short time afterwards, it again becomes clear; at this point the acid liquors, which contain π -bromocampa-phoric acid, are poured from the oil, and the latter is once more heated with a small quantity of nitric acid of the strength originally used, in order to ensure the conversion of any, as yet, unaltered π -di-bromocampa-phor. The oil is now washed with successive small quan-tities of water, then with a dilute solution of sodium carbonate, and finally with water. After this treatment, it gradually assumes a semi-solid character, due to partial crystallisation, and, at the end of several days' time, it is spread on porous porcelain, which absorbs some oily matter, and leaves a nearly white, crystalline powder. When quite dry, the powder is transferred to a flask, and shaken with cold, light petroleum (b. p. 25–50°), in which the greater part dissolves, only the π -dibromocampa-phor which has escaped nitration being insoluble; the latter is then separated by filtration, and the solution allowed to evaporate in a cool spot as slowly as possible; if the temperature be sufficiently low, the substance separates in the form of long, flat, colourless crystals, but in the majority of cases, it is deposited as a clear, colourless oil, which is, nevertheless, pure enough for further treatment.

A sample of the crystalline product, which had been further puri-fied by recrystallisation, was dried over sulphuric acid and analysed; it proved to be a *dibromonitrocampa-phor*.

0.1863 gave 0.2292 CO_2 and 0.0696 H_2O . C = 34.00; H = 4.22.

0.1605 „ 0.1718 AgBr. Br = 45.18.

$\text{C}_{10}\text{H}_{13}\text{Br}_2\text{NO}_2$ requires C = 33.80; H = 3.66; Br = 45.07 per cent.

$\alpha\pi$ -Dibromo- α -nitrocamphor crystallises from cold petroleum in flattened, colourless, transparent needles, which melt at 54° . It may also be recrystallised from hot methylic alcohol by cooling, if the operation be quickly carried out, but a considerable quantity of the substance is lost by decomposition during the evaporation of the mother liquors; it is excessively soluble in acetone, benzene, and chloroform, and cannot be recrystallised from those solvents; in petroleum, it is also readily soluble, but less so than in the solvents just referred to.

Dibromonitrocamphor is exceedingly prone to decomposition, and is slowly decomposed when dissolved in ethylic or methylic alcohol or in acetone, a yellow oil gradually making its appearance, and irritating vapours being evolved. When heated, it slowly assumes a reddish-brown hue, and at 195° effervesces, evolving coloured gases, which apparently consist of a mixture of bromine and oxides of nitrogen. The residue is a yellowish oil, from which no crystalline substances have been obtained.

The crystals deposited from a light petroleum solution are long, flat needles, whose faces are perfectly flat, and give good images; the ends of the crystals, however, are invariably devoid of faces, being serrated, and frequently hollowed out in a curious manner. They appear to belong to the anorthic system, the extinctions in polarised light making about 12° with the edge. A few fragments of the crystals may be obtained, which show in convergent polarised light an optic axial picture. The axial angle is large, the double refraction being positive in sign and weak; the dispersion is strong.

$\alpha\pi$ -Dibromo- α -nitrocamphor is isomeric with the nitro- β -dibromocompound described by Kachler and Spitzer (*Monatsh.*, 1882, **3**, 218).

π -Bromo- α -nitrocamphor, $C_{10}H_{14}BrNO_3$.

$\pi\alpha$ -Dibromo- α -nitrocamphor is not sensibly affected in neutral alcoholic solution by the zinc-copper couple, or by aluminium amalgam, differing in this respect from $\alpha\alpha$ -bromonitrocamphor, which, under these conditions, is reduced to α -nitrocamphor with ease. It is attacked, however, by aqueous or alcoholic alkali, the use of the former resulting in the production of a jelly-like mass of salts which coats the dibromonitrocamphor, and thus prevents further action; alcoholic potash, on the other hand, is not subject to this disadvantage, consequently the following method was finally adopted for the reduction of the compound to π -bromo- α -nitrocamphor.

The crude dibromonitrocamphor is dissolved in about five times its weight of methylated spirit, warmed on the water bath, and an aqueous solution of the calculated quantity of potash (two molecular proportions) is then added, whereupon the liquid at once assumes a

brown tint, which gradually deepens. After the lapse of an hour or so, the whole is poured into water, and the mixture of unaltered dibromonitrocampbor and dibromocampbor, which appears as an oil, is separated from the solution, and treated afresh. The clear solution is filtered and mixed with an excess of sulphuric acid, when the bromonitrocampbor is precipitated as an oil, which changes almost at once to a crystalline powder, if the treatment with potash has not been carried too far; the solid is then filtered from the aqueous solution, which contains some quantity of organic compounds of an acidic character, and purified by crystallisation from hot ethylic acetate, the crystals being subsequently washed with ether, in which the accompanying resinous matter is readily soluble.

A sample purified in this way, and dried at 100° , was analysed.

0.1632 gave 0.2586 CO_2 and 0.0748 H_2O . $\text{C} = 43.21$; $\text{H} = 5.09$.

0.2066 „ 0.1434 AgBr. $\text{Br} = 29.5$.

$\text{C}_{10}\text{H}_{14}\text{BrNO}_3$ requires $\text{C} = 43.47$; $\text{H} = 5.07$; $\text{Br} = 28.9$ per cent.

The crystallographic properties of π -bromo- α -nitrocampbor are of considerable interest. It is trimorphous, and crystals of three distinct modifications have been obtained, of which two were of sufficient magnitude for goniometrical measurement.

When the substance is crystallised from alcohol, dilute acetic acid, or acetone, it appears as long needles, belonging to the orthorhombic system. The same modification is obtained from a mixture of ethylic acetate and light petroleum as elongated, six-sided, opaque plates. It melts pretty sharply at 126° , and, after solidification, the melting point is unaltered. It may be obtained on a microscope slide by melting any of the modifications beneath a cover glass, and allowing the slide to cool. On examination in convergent polarised light, an optic axial bisectrix, probably the acute, is found to be perpendicular to the slide. The optic axial angle is moderately wide, the double refraction very weak, and positive in sign; the dispersion is strong.

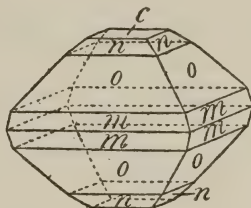
A second modification may be obtained in the following manner. The substance is dissolved in the smallest possible quantity of cold chloroform, and an equal bulk of ethylic acetate is added to the solution; the mixture, on being allowed to evaporate spontaneously, deposits transparent, pyramidal crystals of considerable size, frequently measuring 5 mm. in diameter. A fragment of one of these crystals when placed in a capillary tube melts quite sharply at 108° ; if, however, the crystals be first crushed, the melting point may lie anywhere between this temperature and 120° . In any case, the mass after solidification melts once more at 126° , the melting point of the first modification. The crystals belong to the tetragonal system, and have been goniometrically measured.

Crystalline form : Tetragonal.

$$a : c = 1 : 1.1002.$$

Forms observed: $c\{001\}$, $o\{101\}$, $m\{304\}$, $n\{301\}$.

FIG. 1.



The following angular measurements were obtained.

Angles.	No. of observations.	Limits.	Mean.	Calculated.
$oc = 101 : 001$	24	$47^\circ 17' - 48^\circ 7'$	$47^\circ 44'$	—
$oo = 101 : 10\bar{1}$	12	$84 21 - 85 1$	$84 33$	$84^\circ 32'$
$em = 001 : 304$	8	$39 28 - 39 34$	$39 31$	$39 32$
$en = 001 : 301$	6	$72 53 - 73 23$	$73 9$	$73 9$
$mo = 304 : 101$	10	$7 27 - 8 40$	$8 20$	$8 12$
$nn = 301 : 30\bar{1}$	4	$33 5 - 34 10$	$33 20$	$33 43$
$on = 001 : 301$	8	$25 5 - 26 15$	$25 36$	$25 25$
$mn = 304 : 301$	4	$33 10 - 33 54$	$33 24$	$33 36$
$oo = 101 : 011$	16	$62 29 - 63 44$	$63 2$	$63 6$
$om = 101 : 034$	8	$58 16 - 59 18$	$58 43$	$58 45$
$on = 101 : 031$	2	$78 36 - 79 16$	$78 56$	$78 45$

Although the observed and calculated values are in many cases in fair agreement, this circumstance can only be regarded as fortuitous, as the limits are wide, owing to the poorness of the images, and the number of measurements is small, so that the probable error is considerable.

As these crystals are combinations of simple tetragonal forms, a second series of indices may be chosen, namely $c\{001\}$, $o\{111\}$, $m\{334\}$, and $n\{331\}$. In this case, the axial ratio will become $a : c = 1 : 7780$.

The form $c\{001\}$ is present on nearly all the crystals, and is usually small and bright; the forms $o\{101\}$ and $m\{304\}$ occur in the majority of cases, but either may be entirely or partly missing; the form $n\{301\}$ is found on few of the crystals, and is usually small and dull. Although some of the faces making up the forms $o\{101\}$, $m\{304\}$, and $n\{301\}$ are frequently absent, yet no regularity has been observed, such as would be expected were their absence due to hemihedrism.

There appears to be a cleavage parallel to $c\{100\}$, as through most crushed fragments a uniaxial interference figure may be seen in the

centre of the field when examined in convergent polarised light; the double refraction is negative in sign, and strong.

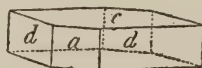
A third modification is deposited from a solution of π -bromo- α -nitrocamphor in chloroform, on spontaneous evaporation. The crystals are of smaller size than those of the last form, but allow of more exact measurement, as the faces are comparatively bright. Like the first-mentioned form, it belongs to the orthorhombic system. A small crystal, when placed in a capillary tube, melts quite sharply at 142° ; if crushed, however, the melting point is usually about 6° lower, but is not a constant factor. When re-heated, the melting point is that of the first modification, namely, 126° .

Crystalline System: Orthorhombic.

$$a : b : c = 1.2159 : 1 : ?$$

Forms observed: $a\{100\}$, $d\{110\}$, $c\{001\}$.

FIG. 2.



The following angular measurements were obtained.

Angle.	No. of observations.	Limits.	Mean.	Calculated.
$ad = 100 : 110$	32	$50^\circ 0' - 51^\circ 13'$	$50^\circ 34'$	—
$dd = 110 : \bar{1}10$	28	$78 16 - 79 36$	$78 52$	$78^\circ 52'$
$ad = 100 : 1\bar{1}0$	32	$49 57 - 51 6$	$50 32$	$50 34$
$ac = 100 : 001$	12	$89 38 - 90 29$	$89 58$	$90 0$
$dc = 110 : 001$	10	$89 40 - 90 32$	$89 59$	$90 0$
$dc = 110 : 00\bar{1}$	10	$89 28 - 90 20$	$90 1$	$90 0$

The crystals are colourless, transparent plates, of about 3 mm. in length. The form $a\{100\}$, which is frequently absent, and $d\{110\}$ are usually small and bright; $c\{001\}$, naturally the largest, is nearly always pitted, giving multiple images.

The optic axes emerge through $d\{110\}$, nearly perpendicularly, $c\{001\}$ being therefore parallel to the optic axial plane, the axis b being the acute bisectrix, and the magnitude of the axial angle about 79° .

The double refraction is positive in sign and weak, and the dispersion is weak. The cleavage is parallel to $a\{100\}$.

A solution containing 1.7308 gram of π -bromo- α -nitrocamphor in 25 c.c. of chloroform, examined in a 2-decimetre tube at 18° , gave, as a mean of 24 concordant measurements, $\alpha_D = 4^\circ 57'$, whence the specific rotatory power $[\alpha]_D = 33.0^\circ$.

π -Bromo- α -nitrocamphor behaves as a strong acid. Being only slightly soluble in water, it reddens litmus very slowly, but it decomposes hot solutions of alkali carbonates, with the formation of salts and the evolution of carbonic anhydride. Its salts are very characteristic.

The *potassium* salt is prepared by dissolving the substance in a hot concentrated solution of potassium carbonate, from which it crystallises in colourless needles, on cooling. It is readily soluble in water, acetone, and hot alcohol, separating from the latter, on cooling, in crystals resembling those deposited from the aqueous solution. The latter were dried in the air, and analysed.

0.1734 lost 0.0178 H_2O at 150° , and gave 0.0423 K_2SO_4 . $\text{H}_2\text{O} = 10.26$; $\text{K} = 10.91$.

$\text{C}_{10}\text{H}_{13}\text{NO}_3\text{BrK} \cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 10.28$; $\text{K} = 11.14$ per cent.

The salts of *ammonium* and *sodium* resemble that of potassium.

The *barium* salt is obtained on adding a solution of barium hydroxide to a dilute alcoholic solution of the nitro-compound, or by the addition of barium chloride to the aqueous solution of the potassium salt. It forms long, glistening needles, and is practically insoluble in water.

A specimen was analysed.

0.1761 lost 0.0159 H_2O at 150° , and gave 0.0594 BaSO_4 . $\text{H}_2\text{O} = 9.03$; $\text{Ba} = 17.83$.

$(\text{C}_{10}\text{H}_{13}\text{NO}_3\text{Br})_2\text{Ba} \cdot 4\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 9.51$; $\text{Ba} = 18.05$ per cent.

From aqueous solutions of the potassium salt, the following metallic salts may be obtained by double decomposition.

The *calcium* salt, precipitated by means of calcium chloride, is a white, micro-crystalline precipitate resembling the barium salt. The *copper* salt, obtained as a voluminous, flesh-coloured precipitate, gradually changes, when kept, to a mass of long, flexible, pink, needles. It is insoluble in cold water and alcohol, but dissolves very readily in acetone; its solution in the latter, on spontaneous evaporation, deposits the salt in the form of transparent, orange plates of considerable size. The *manganese* and *zinc* salts are obtained as colourless, bulky precipitates, which, under the microscope, are seen to consist of tufts of minute needles. The *nickel* salt is precipitated as a nearly white, amorphous mass; it dissolves sparingly in hot water, and is deposited, on cooling, in an amorphous condition. The *cobalt* salt behaves in a striking manner. When solutions of cobalt nitrate, and potassium bromonitrocamphor are mixed, they give a *flesh coloured* precipitate, which, under the microscope, shows no trace of crystalline matter. After the lapse of a few minutes, however, the colour of the mass gradually changes to a *bluish-purple*, the

change being accompanied by the assumption of a crystalline habit. The change from the flesh-coloured, amorphous mass to a magma of blue needles may be readily traced under the microscope. The salts of *bismuth* and *lead* are colourless, amorphous compounds, those of *aluminium*, *mercury*, and *magnesium* being very soluble in water.

With solutions of ferric salts, a brilliant, purple coloration is produced, but no precipitate; this behaviour recalls that of the hydrate of α -nitrocamphor, described by Cazeneuve (*loc. cit.*).

In evidence of the strongly acidic nature of π -nitro- α -bromocamphor, it may be mentioned that an alcoholic solution of the substance acts on iron with considerable rapidity, the brilliant purple colour above referred to being at once produced. A bright steel knife, if dipped into the solution, is at once corroded.

π -Bromo- α -nitrocamphor is not attacked by dilute nitric acid to any great extent. If, however, it be covered with fuming nitric acid and warmed on the water bath, energetic oxidation is effected, attended by copious evolution of red fumes. The clear solution, on cooling, deposits a crystalline acid, which is almost insoluble in cold water, but dissolves readily in hot. It melts at 214–215°, and is the π -bromocamphoric acid (m. p. 217°) already obtained by one of us (*Proc.*, 1895, 33), as, on mixing it with that substance, its melting point is not depressed. Its identity with the latter compound was put beyond doubt by preparing from it, by the action of sodium carbonate, the acid of the composition $C_{10}H_{14}O_4$, melting at about 165° (*Proc.*, 1895, 88).

In order to ascertain whether π -bromo- α -nitrocamphor behaved as a saturated compound, a trace of bromine was added to its solution in chloroform, but the colour underwent no change even after several days; its sodium salt, in aqueous solution, did not destroy the colour of dilute permanganate for a considerable period.

In view of the fact that the isomeric π -bromonitrocamphor was readily converted into an acetate by acetyl chloride, the behaviour of the parent substance towards acetylating agents was carefully studied; it was found that after many hours boiling, either with acetyl chloride or acetic anhydride, practically the whole of the π -bromo- α -nitrocamphor could be recovered unchanged, a minute quantity only of an oily substance, insoluble in alkalis, being produced.

Reduction of π -Bromo- α -nitrocamphor.—Attempts to obtain the corresponding bromamidocamphor from this substance resulted in the formation of several compounds, the nature of the product depending entirely on the method employed.

When a warm alcoholic solution of the nitro-derivative is mixed with one of stannous chloride in hydrochloric acid, immediate action

occurs, as no precipitate is produced on pouring the solution into water; the stannous chloride, however, does not undergo oxidation, and after precipitating the tin and subsequently evaporating the solution, the presence of an amido-compound cannot be detected; the sole product under these conditions is the isomeric bromonitro-camphor described later.

Reduction by means of zinc dust and acetic acid gives different results. A few grams of the nitro-compound were dissolved in a small quantity of acetic acid and mixed with successive portions of zinc dust; as the metal gradually became coated with zinc acetate, the solution was heated on the water bath to assist dissolution, but the reduction was only completed after three days; the solution was then diluted, the zinc precipitated by hydrogen sulphide, and the solution evaporated nearly to dryness. The acetic acid was next expelled by repeatedly evaporating with hydrochloric acid, and the residual hydrochloride was finally dissolved in a mixture of alcohol and ether; in the course of a few hours, the cold solution deposited a small quantity of a crystalline substance, which was filtered off, and recrystallised from alcohol. This compound is the *hydrochloride* of an *amidocamphor* and appears to be identical with the substance obtained by Schiff on reducing ordinary α -nitrocamphor. It is very soluble in water, and crystallises from alcohol in nearly colourless needles, which blacken above 220° , and melt a little later; when heated with alkalis it gives off a base with a strong ammoniacal odour; if chloroform is added to the solution containing alkali, the presence of an isocyanide may be at once detected by its smell. When the hydrochloride is treated in aqueous solution with silver nitrate, silver chloride is at once precipitated, and, on the addition of ammonia, the solution gradually becomes black, especially if warmed; this is due no doubt to the production of metallic silver. The *platinochloride* crystallises in brownish-yellow needles.

Analysis of the hydrochloride shows that bromine is not present, a determination of the chlorine by the Carius method giving the same percentage as that obtained by direct precipitation.

0.1167 gave (by Carius' method) 0.0827 gram AgCl. Cl = 17.53.

0.1114 „ (by precipitation) 0.763 gram AgCl. Cl = 17.16.

$C_{10}H_{15}O \cdot NH_2, HCl$ requires Cl = 17.44 per cent.

As in this experiment the reduction had evidently been carried too far, further attempts were made to reduce the nitro-group without displacing the bromine by hydrogen. The acetic acid was therefore taken in large excess and the zinc dust added in very small increments, the whole operation being conducted in the cold. After the lapse of about nine hours, the liquid was poured into water and the

filtered solution treated as before. In one instance only, a small quantity (0.6 gram) of the hydrochloride of an amine which contained bromine was obtained; but this amine did not correspond with the nitro-compound taken, as it was identical with the base obtained from the isomeric bromonitrocamphor described later. It is probable, therefore, that the bromonitrocamphor had undergone change into its isomer, with subsequent reduction.

π -Bromo- α -amidocamphor.

The production of the looked for amido-compound was effected only by the aid of sodium amalgam, the method finally adopted leaving little to be desired. A solution of π -bromo- α -nitrocamphor in dilute aqueous soda is placed in a stoppered bottle with a small quantity of sodium amalgam, and the whole continually shaken. After a few minutes, a yellowish oil makes its appearance, and is at once extracted with a little ether, which is then separated and replaced by a fresh portion, the process being repeated until the ethereal extracts, on evaporation, leave no appreciable residue. The oil thus obtained consists for the most part of the desired amine, which gradually separates in small crystals from the oily liquors; in a week or two, the semi-crystalline mass may be spread on porous porcelain, and allowed to drain. The residual waxy mass is a mixture of two substances, namely, the amine described below, and another base, present in much smaller quantity, but which must be separated from the former by fractional crystallisation, using ethylic acetate and benzene alternately, and may readily be distinguished from the first-mentioned base, which crystallises in plates, by its needle-like habit.

π -Bromo- α -amidocamphor crystallises from ethylic acetate in large, colourless, transparent, monoclinic plates, melting at 159° ; on account of its solubility in this solvent, the faces are generally rounded and give no definite images; there is no definite cleavage. When the substance is melted on a glass slide beneath a cover-glass, it solidifies rapidly from numerous centres, on cooling, forming an area made up of ill-defined patches. Through many places, the acute optical bisectrix emerges normally to the slide. The axial angle is moderately large, the double refraction being positive in sign and weak; the dispersion is very weak.

It dissolves readily in alcohol, and is reprecipitated from the solution in glistening six-sided plates; it is also very soluble in benzene, ether, and chloroform, but less easily in petroleum. It is very slightly volatile in steam, to which it does not impart any characteristic odour, as do the isomeric π -bromo-amidocamphor and

amidocamphor. It does not volatilise to any great extent when heated, but gradually darkens and decomposes, finally forming a charcoal-like mass. It evolves only a faint odour of carbylamine when treated with chloroform and caustic potash.

The *hydrochloride*, which may be readily obtained in a pure state from the crude oil, is very soluble in alcohol, and may be reprecipitated from its solution by the addition of ether; when prepared in this manner, it forms glistening needles, which darken slowly on heating, and melt and decompose at about 220° . It dissolves slowly in water, and the solution, when boiled, gradually decomposes, the free base being deposited. The crystals of the salt from alcohol were washed with ether, heated at 100° , and analysed.

0.2515 gave 0.3921 CO_2 and 0.1365 H_2O . $\text{C} = 42.55$; $\text{H} = 6.04$.

0.0952 substance (by Carius' method) gave 0.1095 $\text{AgCl} + \text{AgBr}$.
 $\text{Br} + \text{Cl} = 40.08$.

0.2272 substance (on boiling with silver nitrate and nitric acid) gave 0.1167 AgCl . $\text{Cl} = 12.70$.

$\text{C}_{10}\text{H}_{14}\text{BrO}\cdot\text{NH}_2\cdot\text{HCl}$ requires $\text{C} = 42.47$; $\text{H} = 6.02$; $\text{Br} + \text{Cl} = 40.88$; and $\text{Cl} = 12.56$ per cent.

The *oxalate*, made by mixing alcoholic solutions of oxalic acid and the base, crystallises in minute, well-defined, four-sided plates, which melt at 200 — 201° , and are very slightly soluble in alcohol and water. The *platinochloride* may be prepared by precipitating a strong solution of the base in strong hydrochloric acid, with platinum tetrachloride. It is deposited as a jelly on standing, which should be separated, dried, dissolved in alcohol, and reprecipitated by the addition of ether and light petroleum; the salt is thus obtained as attenuated, glistening needles, which are excessively soluble in alcohol and water, but insoluble in ether; when heated, they blacken at 210° , melting and decomposing at 220° .

The *acetyl* derivative is readily formed on treating the base with acetyl chloride; it separates from dilute alcohol in thin leaflets, melting at 167 — 168° : it is readily soluble in alcohol, and dissolves to some extent in hot water.

π -Bromo- α -isonitrocamphor.

This substance, as has already been mentioned, was obtained in small quantities by the action of a solution of stannous chloride in hydrochloric acid on the alcoholic solution of the original nitro-compound. The analyses at first made with the hydrated substance (which had been crystallised from water) gave results which for some time misled us with regard to the true nature of the substance, which we supposed to be a reduction product. The discovery that the tin used in its pro-

duction had not undergone oxidation, led us to try the action of concentrated hydrochloric acid alone on π -bromo- α -nitrocamphor. The following is the most convenient method for preparing the compound.

The nitro-compound is placed in a flask with five times its weight of strong hydrochloric acid, and the mixture warmed on the water-bath, when the substance gradually liquefies, and nearly all dissolves, forming a dark-coloured solution, which finally becomes nearly colourless. The liquid is then decanted from a small quantity of tarry matter, and allowed to cool, the side of the vessel being scratched to promote crystallisation; a nearly colourless crystalline compound is then deposited, and a further quantity may be obtained on evaporating the mother liquors. The crude product may be purified by recrystallisation from hot water, benzene or chloroform.

Analyses of samples obtained from aqueous solution, and dried in the air, gave results agreeing with those required for a mon-hydrated bromonitrocamphor.

0.1632 gave 0.2458 CO_2 and 0.0812 H_2O . C = 41.07; H = 5.53.

0.1620 „ 0.2436 „ 0.0797 „ C = 41.01; H = 5.47.

0.1087 „ 0.0699 AgBr. Br = 27.32.

$\text{C}_{10}\text{H}_{16}\text{BrNO}_4$ requires C = 40.82; H = 5.45; Br = 27.21 per cent.

Crystals of the substance which had been obtained from chloroform proved, on analysis, to be anhydrous.

Found C = 43.57; H = 5.32.

$\text{C}_{10}\text{H}_{14}\text{BrNO}_3$ requires 43.47; H = 5.07 per cent.

π -Bromo- α -isonitrocamphor differs from its isomer in many respects, as, for example, in being comparatively readily soluble in water. The aqueous solution has a strongly acid reaction towards litmus, but when cold does not decompose carbonates as readily as dilute mineral or carboxylic acids do. It crystallises from hot water in transparent, colourless leaflets, which contain water of crystallisation, and melt at some point between 109° and 112° , according to the speed with which the temperature is raised; after solidification they melt at 134 — 136° . The aqueous solution gradually assumes a pink colour when exposed to the air.

The anhydrous substance is readily soluble in chloroform and benzene, from which it is deposited in small, colourless needles, melting sharply at 137 — 138° ; in alcohol and acetone, it is more readily soluble, but it is nearly insoluble in petroleum. It is scarcely soluble in cold ethylic acetate, but dissolves readily when hot, the solution, on cooling, depositing the compound in transparent plates of considerable size; these crystals melt at 122° , effervescence being at once apparent, but after the substance has solidified the melting

point is $134-136^\circ$. This change in melting point is not due to dimorphism, but to included ethylic acetate, which is not set free until the crystals are fused.

The small crystals from chloroform, &c., melting at $137-138^\circ$, are flattened orthorhombic plates, having the optic axial plane parallel to the large face; they are obliquely truncated at their ends by other faces, and the crystals thus appear six-sided. The large crystals from ethylic acetate are also flat, orthorhombic plates or prisms, having the optic axial plane parallel to the largest face, but instead of being obliquely truncated, the terminal edges are set at right angles to the others, so that the crystals form four-sided rectangular plates. The cleavage is perfect, and parallel to the larger pinacoid. The optic axial angle is moderately large; the double refraction is positive and strong, the dispersion being weak.

To determine the specific rotation of the substance, 1.7694 grams were dissolved in 25 c.c. of chloroform, and examined at 18° in a 2-decimetre tube. The rotation α_D was found to be $+7^\circ 27'$ as a mean of 24 concordant measurements, giving $[\alpha]_D = +52.7^\circ$.

This π -bromo- α -isonitrocamphor, like its isomeride, has a strongly marked acidic character, and forms characteristic salts, which are, as a rule, more readily soluble than those of the isomeride.

The potassium salt is obtained by warming a few grams of the nitro-compound with enough strong caustic potash solution (sp. gr. 1.3) to cause complete dissolution; on cooling, the salt separates as a mass of colourless needles. It is excessively soluble in water, and dissolves readily in hot alcohol, from which it separates in anhydrous, white needles.

0.3083 gave 0.0865 K_2SO_4 . $K = 12.58$.

$C_{10}H_{13}BrNO_3K$ requires $K = 12.42$ per cent.

The *barium* salt, made by adding a large excess of baryta-water to an aqueous solution of the nitro-compound, is deposited in the form of microscopic crystals, tending to aggregate and form clots. It is practically insoluble in water. A specimen was dried in the air and analysed.

0.1624 lost 0.0087 H_2O at 120° , and gave 0.0532 $BaSO_4$. $Ba = 19.25$;
 $H_2O = 5.35$.

$(C_{10}H_{13}BrNO_3)_2Ba \cdot 2H_2O$ requires $Ba = 18.95$; $H_2O = 4.98$ p. c.

The *calcium* salt resembles the barium salt in appearance and solubility. Salts of magnesium and zinc give no precipitates when their solutions are added to that of the above potassium salt. Neutral lead acetate, in like manner, affords no insoluble lead salt, but the basic acetate gives a white precipitate, insoluble in boiling water. The *cobalt* salt of the isonitro-compound is obtained in the usual

manner as an amorphous pink precipitate, which gradually changes to a mass of red needles. The *nickel* and *mercuric* salts are white and amorphous; the former dissolves readily in hot water, separating again on cooling as a greenish amorphous crust. The *copper* salt is blue, and dissolves readily in water, differing, therefore, from the copper salt of the original nitro-compound, which is pink, and is quite insoluble in water. The *bismuth* salt crystallises from hot water, in which it is readily soluble, in the form of glistening white needles.

In solutions of the potassium salt, ferric chloride produces a yellowish-brown coloration, so that this reagent serves as a test of the purity of the isonitro-compound, a trace of its isomer producing at once a distinct purple colour.

When π -bromo- α -isonitrocamphor is heated with fuming nitric acid, it undergoes no great change, the substance merely liquefying, and it may be ultimately recovered, even after some hours; if, however, the nitric acid is more dilute (sp. gr. = 1.3), it dissolves at once, and, after half an hour's boiling, the solution, as it cools, deposits minute, well-defined crystals. These melt at 215° , and are practically pure π -bromocamphoric acid.

In order to determine whether the nitro-derivative was unsaturated, its behaviour towards bromine, in weak solution, and dilute potassium permanganate was studied. It was found that in chloroform solution the colour imparted by a trace of bromine was not destroyed, even after two days' time; moreover, a dilute solution of potassium permanganate was only decolorised slowly by a faintly alkaline solution of the sodium salt.

Behaviour of π -Bromo- α -isonitrocamphor with Acetyl Chloride.—When this substance is added to acetyl chloride, interaction occurs, and bubbles of hydrogen chloride are slowly given off; the action may be completed by warming the mixture on the water-bath during 30 minutes. On pouring the solution into cold dilute soda, a white, crystalline precipitate is obtained, only sparingly soluble in alcohol, and even less readily in ethylic acetate, benzene, or ether; it appears to be quite insoluble in hot water. It was crystallised from alcohol, dried at 100° , and analysed. The results agreed with those required by a monacetyl derivative of a nitrobromocamphor.

0.2012 gave 0.3360 CO_2 and 0.0974 H_2O . C = 45.54; H = 5.37.

$\text{C}_{12}\text{H}_{16}\text{BrNO}_4$ requires C = 45.28; H = 5.03 per cent.

Acetyl- π -bromo- α -isonitrocamphor crystallises from alcohol in elongated, six-sided, orthorhombic plates, the optic axial plane being parallel to the large face.

Reduction of π -Bromo- α -isonitrocamphor.—The experiments made with the original nitro-compounds having served to show that sodium

amalgam was the most suitable reducing agent, attempts were made to effect the reduction of its isomer by a similar process. It was found, however, that reduction took place to a very slight extent, if at all; and other reducing agents which were tried also failed to give the desired amido-compound, except in small quantities. In one experiment, however, a dilute solution of the substance in acetic acid was shaken at intervals during a week, with a large excess of zinc-dust; the solution was then filtered, saturated with hydrogen sulphide, separated by filtration from zinc sulphide, and evaporated. An oily residue was thus obtained, which, on heating with caustic soda, evolved an ammoniacal odour. It was therefore evaporated two or three times with hydrochloric acid, the oily product dissolved in alcohol, and the solution mixed with several times its bulk of ether; the substance which was subsequently deposited proved to be the hydrochloride of a base, identical with that obtained by a somewhat similar treatment of the original nitro-compound. The following observations were made with the specimen first prepared, the quantity of that obtained in the second instance serving merely for the purpose of identification.

The *base* itself was not isolated; it was found, however, that if the crystals of the hydrochloride were covered with strong ammonia, they disappeared, and were replaced by a waxy substance, readily soluble in water and in ether; this in all probability was the free bromisoamidocamphor.

The *hydrochloride* is excessively soluble in water, and rather soluble in ethylic alcohol; from the latter, it separates in the form of long, colourless, transparent needles, which appear to contain water of crystallisation, as when exposed to the air they gradually become opaque, finally falling to a white powder. Like most amine hydrochlorides, it has a tendency when in solution to undergo slight decomposition, gradually becoming dark brown. When heated with chloroform and caustic potash, it evolves a pungent odour, resembling that of carbylamines. When boiled in ammoniacal solution with silver nitrate, it reduces the latter, metallic silver being deposited. When slowly heated, it melts, and decomposes at $238-239^{\circ}$.

A determination of the halogen (I) by Carius' method, and (II) an estimation of the chlorine by direct precipitation with silver nitrate, gave the following results.

I. 0.1037 gave 0.1222 AgCl + AgBr. Cl + Br = 41.06.

II. 0.0495 „ 0.0262 AgCl. Cl = 13.09.

$C_{10}H_{14}OBr \cdot NH_2 \cdot HCl$ requires Cl + Br = 40.88; Cl = 12.57 per cent.

The *platinochloride* is obtained as a pale-yellow, granular precipitate on adding platinum tetrachloride to a solution of the hydro-

chloride. It is soluble in water and alcohol, being deposited from the latter in the form of transparent, yellow, or brownish-yellow octahedra. It melts and decomposes at 220—230°.

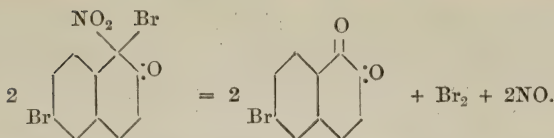
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XXXII.—*Note on the Formation of Camphorquinone from α -Chloronitrocamphor.*

By ARTHUR LAPWORTH, D.Sc.

DURING the course of the examination of $\pi\alpha$ -dibromonitrocamphor, undertaken by the author in conjunction with Dr. Kipping, it was observed that this substance undergoes a sudden and somewhat violent decomposition when heated, nitrous fumes, mixed with bromine, being evolved. The product was obviously a mixture, but its study was out of the question, owing to the difficulty of obtaining sufficient material for investigation. As any facts relating to the properties of camphor derivatives are of interest, it was thought worth while to examine the behaviour of the analogous α -bromonitrocamphor and α -chloronitrocamphor, which may be readily obtained in quantity. On referring to the literature on the subject, it was found that Cazeneuve and Morel (*Bull. Soc. Chim.*, 1885, **44**, 165) had already stated that these substances are decomposed by heat, nitrous fumes and halogen being liberated. The examination of the products, however, was not carried out, or failed to yield any results of interest.

α -Bromonitrocamphor, $C_{10}H_{14}BrO(NO_2)$, is known to contain the group $-CBr(NO_2)\cdot CO-$; it is non-acidic, but on reduction yields α -nitrocamphor, $C_{10}H_{15}O\cdot NO_2$, which possesses a marked acidic character, and, therefore, contains the group $-CH(NO_2)-$, the latter substance on oxidation yielding camphoric acid, $C_8H_{14}(COOH)_2$. α -Bromonitrocamphor is, therefore, in this respect analogous in constitution to the bromonitroketonaphthalenes obtained by Armstrong and Rossiter (*Proc.*, 1887, 144), by acting on 1 : 2-bromonaphthols with fuming nitric acid. These compounds, like α -bromonitrocamphor, lose bromine on reduction, yielding nitro-derivatives; when they are heated, both bromine and nitric oxide are evolved, the corresponding 1 : 2-diketocompounds or β -naphthaquinones being produced. Thus, 1 : 3' : 2-dibromonaphthol, on treatment with nitric acid, gave a dibromonitroketonaphthalene, which finally afforded 3'-bromo- β -naphthaquinone.



If α -bromonitrocamphor were to decompose in like manner, it should yield camphorquinone, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{CO} \end{array}$. This substance has already been prepared, and fully characterised by Claisen (*Ber.*, 1889, 22, 530), who obtained it from isonitrosocamphor by two methods, namely, by the action of nitrous acid, and by heating it first with sodium hydrogen sulphite, and subsequently with dilute sulphuric acid.

The decomposition of α -bromonitrocamphor was found to be almost explosive in character; the product was oily, and appeared to contain very little of the expected substance. The examination of α -chloronitrocamphor, on the other hand, gave more satisfactory results, and, as its decomposition took place less suddenly, it was chosen for examination. The product obtained from it was a black, tarry solid which, on distillation, yielded an orange-coloured, waxy mass; this, on standing, became bespangled with minute, yellow crystals, but it was found impossible to separate the quinone by fractional crystallisation; ultimately, however, the following method of separation was devised, which yielded a small quantity of the quinone in a pure condition.

α -Chloronitrocamphor was introduced into a capacious retort in quantities of not more than 2 grams at a time, heat being applied after each addition, and the heating was continued until the vigorous disengagement of gases was at an end; the retort was finally heated during several hours at 200° in a sulphuric acid bath, and was then allowed to cool. The charred mass after being boiled in a small quantity of alcohol, was shaken with a hot strong solution of sodium hydrogen sulphite, filtered from tarry matter, and the dark coloured liquid extracted with successive small quantities of ether, which dissolved a considerable amount of volatile nitrogenous matter soluble in water. On acidifying with sulphuric acid the solution of the bisulphite compound of the quinone, and distilling with steam, the whole of the quinone volatilised within the first few minutes. It was then collected and repeatedly crystallised from alcohol. The yield was less than 5 per cent. of the original α -chloronitrocamphor.

A specimen purified in the manner described was dried over sulphuric acid, sublimed, and analysed.

0.2044 gave 0.5406 CO_2 and 0.1588 H_2O . C = 72.1; H = 8.6.

$\text{C}_{10}\text{H}_{14}\text{O}_2$ requires C = 72.3; H = 8.4 per cent.

The substance crystallised from alcohol in bright yellow, glistening needles or flattened prisms, and melted at 196—198° (Claisen gives 198°). It dissolved readily in hot alcohol, in ether, but only sparingly in hot water, and the hot aqueous solution had a characteristic odour reminiscent of camphor. Although the yellow solutions were not decolorised by sulphurous acid, they were when boiled with sodium hydrogen sulphite, the yellow tint appearing again on boiling with dilute sulphuric acid. As indicated above, the quinone volatilised with ease in steam; it sublimed readily below 100°, and even at the ordinary temperature, the apparently amorphous mass gradually becoming covered with glistening, yellow needles. The above properties are exactly those of the quinone described by Claisen, and, in order to establish their identity, a specimen was made by his method; the two were found to be indistinguishable, and, when mixed, the melting point was not depressed. Under convergent, polarised light, the flattened needles of the two specimens were seen to have their optic axial plane parallel to the large face, and to possess, apparently, equally strong double refraction.

The substance obtained from α -chloronitrocamphor when heated with phenylhydrazine in acetic acid solution, yielded a hydrazone which crystallised from alcohol and chloroform in yellow needles melting at 169—171°, the melting point given by Claisen. There can be no doubt, therefore, that camphorquinone is produced from α -chloronitrocamphor by the action of heat, and that the decomposition of the latter substance is, in part, similar to that of the orthobromonitroketonaphthalenes.

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XXXIII.—*The Action of Lead Thiocyanate on the Chlorocarbonates. Part I. Carboxyethylthiocarbimide and its Derivatives.*

By ROBERT ELLIOT DORAN.

AFTER numerous attempts by various chemists to obtain thiocarbimides of the acidic type, their synthesis was first effected by Miquel (*Ann. Chem. Phys.*, 1877, [5], 11, 289), whose method consisted essentially in heating together, under suitable conditions, lead thiocyanate and the corresponding acid chloride; in this way he succeeded in preparing acetyl, butyryl, benzoyl, and salicyl thiocarbimides, two of which, $\text{CH}_3\cdot\text{CO}\cdot\text{NCS}$ and $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NCS}$, were isolated, and their

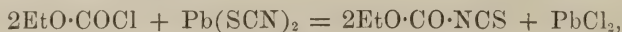
properties examined. In the paper quoted he repeatedly insists on the thiocyanic character of the fatty derivatives; writing, for example, of the acetyl compound, he says:—"This body behaves as a true sulphocyanate, and if the nature of its elements did not place it in the heart of organic chemistry, it might be classed with silicon sulphocyanate, of which it possesses the more general chemical characters." When mixed with aniline, the two substances united directly, affording acetylphenylthiocarbamide, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, and it seems natural to expect that, from such a result, the thiocarbimide function of the substance in question must have been recognised; instead of this, however, the interaction is characterised as "abnormal" (*loc. cit.*, 309 and 318). Several acetylated thioureas and allied compounds have since been obtained by its agency (see, *e.g.*, Dixon, *Trans.*, 1889, **55**, 303 and 304; 1891, **59**, 562, and 1892, **61**, 530); and there now seems no reason to doubt that, in so far at least, as combination with basic substances is concerned, its behaviour is that of a thiocarbimide. Miquel's reaction appears to be generic, the existence of analogous dithiocarbimides, similarly derived from the chlorides of succinic and phthalic acid respectively, having lately been shown (Dixon and Doran, *Trans.*, 1895, **67**, 565) by the preparation of a number of characteristic derivatives; the thiocarbimides themselves, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{NCS})_2$ and $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NCS})_2$, which were obtained only in solution, being apparently too unstable to admit of isolation by the methods commonly employed.* During the course of the joint investigation, the possibility occurred to the writer of obtaining a more highly oxidised class of thiocarbimides by the interaction of lead thiocyanate and the ethereal salts of chlorocarbonic acid; an investigation on these lines was accordingly commenced, of which the results detailed below constituted the first instalment.

Ethyl chlorocarbonate was used for a preliminary experiment, and when a small quantity, dissolved in benzene, was heated with lead thiocyanate there was scarcely any sign of interaction; but, on substituting toluene for benzene, in order to obtain a higher temperature, interaction took place readily, and, after boiling for a few minutes, the solution was found to be free from chlorine, was immediately desulphurised in the cold by ammoniacal silver nitrate, and almost equally easily by alkaline lead tartrate, thus showing the presence of a thiocarbimide.

A larger experiment was now made, using 10 grams of the chlorocarbonate, this was dissolved in anhydrous toluene, and added to

* Further evidence in this direction has also recently been adduced by the production of similar typical compounds (Dixon, *Trans.*, 1895, **67**, 1040) derived from valeryl and cinnamoyl thiocarbimides.

20 grams of lead thiocyanate, an amount somewhat in excess of that required by the equation



and the mixture heated in a reflux apparatus. Interaction commenced before the boiling point was reached, and was complete in 10 minutes, the liquid becoming yellow, and finally bright orange, and the solid buff-coloured. The lead chloride and unchanged thiocyanate were removed by filtration, washing with benzene; both the filtrate and washings thus obtained had lost all smell of the chloro-carbonate, and in its place had a peculiar, pungent, fungus-like odour, whilst its vapour acted very strongly on the eyes.

As the amount of the thiocarbimide, $\text{EtO}\cdot\text{CO}\cdot\text{NCS}$, which could be formed in the above experiment was only slightly more than 17 grams, it was decided to convert the whole of it into derivatives and postpone an attempt to isolate it until some of the latter had been studied. On the assumption, then, that interaction had occurred quantitatively, the benzene-toluene solution, obtained as described, was diluted with the former solvent to a strength equivalent to a gram-molecule per litre, and used up in preparing some of the following derivatives.*

ab-Carboxyethylphenylthiocarbamide, $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

On adding 1.86 grams of aniline, dissolved in benzene, to 2.62 grams of the thiocarbimide, interaction occurred at once, with evolution of heat, and crystals commenced to separate while the liquid was still hot. When cold, the contents of the flask became nearly solid through the further separation of a mass of fine prisms, which, when separated from the mother liquor by filtration, washed with benzene, and dried, were nearly colourless. By recrystallisation from alcohol the substance was obtained in pure white, apparently monoclinic tables, melting without decomposition, at 130° , to a clear liquid, and giving the following figures on analysis.

0.321 gave 0.623 CO_2 and 0.156 H_2O . $\text{C} = 53.23$ p.c. and $\text{H} = 5.4$.
 0.2034 gave 23.0 c.c. moist nitrogen at 20° and 749 mm. $\text{N} = 12.72$.
 0.2497 gave 0.2624 BaSO_4 . $\text{S} = 14.44$.

The formula $\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}_2\text{O}$ requires

	C.	H.	N.	S.	O.
Theory	53.5	5.3	12.52	14.3	14.2
Found	53.23	5.4	12.72	14.44	14.21

* During the course of the investigation, several additional quantities of the thiocarbimide (in solution) were prepared, and in all cases—save where otherwise specified—the solution was used in preparing the various derivatives described.

Properties.—Carboxyethylphenylthiocarbamide is only sparingly soluble in cold, but dissolves freely although slowly in hot alcohol and benzene; it is moderately soluble in cold, and very freely in hot chloroform and carbon bisulphide; sparingly in cold and moderately in hot ether, and is practically insoluble in water. It dissolves in warm dilute potash, but, even after boiling with this reagent, hydrochloric acid precipitates the thiocarbamide unchanged. Its alcoholic solution is at once desulphurised by neutral or ammoniacal silver nitrate, and parts with its sulphur slowly on boiling with alkaline lead solution; if, however, its solution in dilute potash be treated with lead nitrate and warmed, a fine mirror of the corresponding sulphide is at once obtained.

As the composition of this substance establishes the existence (in solution) of carboxyethylthiocarbimide, it was decided to attempt the isolation of the latter, particularly as there were reasons for inferring that it would prove to be moderately stable; but, to secure continuity, an account of the experiments by which this result was effected is deferred for the present.

ab-Carboxyethylbenzylthiocarbamide, $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$.

Interaction, with evolution of heat, occurred at once on mixing benzylaniline (in alcoholic solution) with the thiocarbimide in molecular proportion; no solid separated until the solution was concentrated by evaporation, when a mass of long needles was obtained, which, after recrystallisation from alcohol, melted at $106\cdot5^\circ$ — $107\cdot5^\circ$ to a clear liquid.

0·2014 afforded 0·1942 BaSO_4 or $\text{S} = 13\cdot25$.

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ requires $\text{S} = 13\cdot46$ per cent.

Properties.—Carboxyethylbenzylthiocarbamide is very freely soluble in hot, and moderately freely in cold, alcohol and benzene, very freely in ether and chloroform; freely in hot, and nearly insoluble in cold, light petroleum; very sparingly soluble in water. Its alcoholic solution is slowly desulphurised on heating with alkaline lead solution; with neutral silver nitrate, a white precipitate is thrown down, passing through yellow, orange, and brown to black on heating; with ammoniacal nitrate the same changes occur in the cold.

ab-Carboxyethylorthotolylthiocarbamide,
 $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

2·14 grams of orthotoluidine dissolved in benzene were added to 2·62 grams of the thiocarbimide; interaction, with evolution of heat and separation of solid matter while the mixture was still warm, proceeded exactly as in the case of the phenyl derivative, and after

separation from the mother liquor, washing with benzene, and recrystallising from alcohol, 4 grams were obtained of a pure white product, in long prisms melting at 152.5° , to a clear liquid, without decomposition.

0.2441 gave 0.2402 BaSO_4 . $S = 13.52$.

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ requires $S = 13.46$ per cent.

Properties.—Freely soluble in hot, moderately in cold, alcohol and benzene; moderately in hot, and nearly insoluble in cold, ether; very freely soluble in chloroform. It is also freely soluble in warm dilute potash, this hot solution desulphurising readily on addition of lead nitrate. Its alcoholic solution behaves like that of the phenyl derivative on treatment with other reagents capable of removing sulphur.

ab-Carboxyethylparatolylthiocarbamide,
 $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$.

This derivative resulted from an experiment conducted as above, the same quantities were used, and the course of the interaction was identical, save that the end product was distinctly more soluble in the warm mother liquor. On recrystallisation from benzene, 3.07 grams of the pure thiocarbamide were obtained, in white, glistening, flattened prisms melting at 148 — 149° .

0.2342 gave 0.239 BaSO_4 . $S = 13.62$.

$\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ requires $S = 13.46$ per cent.

Properties.—In respect to its behaviour to solvents and the usual desulphurising agents, carboxyethylparatolylthiocarbamide closely resembles the ortho-derivative.

ab-Carboxyethyl- α -naphthylthiocarbamide,
 $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$.

2.86 grams of α -naphthylamine, in benzene solution, united at once with 2.62 grams of the thiocarbimide; heat was evolved, and a solid separated in fine, granular prisms, which, when collected, washed with and recrystallised from benzene, melted at 183 — 183.5 , without decomposition. 5.2 grams, nearly 95 per cent. of the theoretical yield, of the pure product were obtained.

0.2358 gave 0.20 BaSO_4 . $S = 11.66$.

$\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\text{S}$ requires $S = 11.69$ per cent.

Properties.—Moderately soluble in hot, sparingly in cold, benzene; sparingly in hot, nearly insoluble in cold, alcohol; very freely in hot, and moderately freely in cold, chloroform. Its alcoholic solution parts with its sulphur instantly, and in the cold, to neutral and

ammoniacal silver nitrate, and more readily on heating with alkaline lead solution than any of the preceding derivatives.

ab-Carboxyethyl- β -naphthylthiocarbamide,
 $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_{10}H_7$.

4.76 grams of β -naphthylamine and 4.36 grams of the thiocarbimide respectively, were used; combination, with evolution of heat, occurred as before. The solid, when collected, washed, and dried, weighed 6 grams, and, by recrystallisation from alcohol, was obtained in the form of faintly pink plates, with a pearly lustre, melting at $155-155.5^\circ$, without decomposition.

0.2503 gave 0.2132 $BaSO_4$. $S = 11.71$.

Theory requires $S = 11.69$ per cent.

Properties.—Detailed reference to these is scarcely necessary, they so closely resemble those of the corresponding α -derivative; a slightly greater degree of solubility in the usual solvents was the only difference noted.

ab-Carboxyethylmetaxylylthiocarbamide,
 $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_3(CH_3)_2$.

The above compound was formed with only slight (slow) evolution of heat on mixing the amine, in alcoholic solution, and thiocarbimide in molecular proportion. The contents of the flask became nearly solid, and, on collection and recrystallisation from alcohol, the product was obtained in masses of small, pearly lozenges melting at $152.5-153^\circ$.

0.2175 gave 0.2016 $BaSO_4$. $S = 12.74$.

$C_{12}H_{16}N_2O_2S$ requires $S = 12.71$ per cent.

Properties.—Freely soluble in hot, sparingly in cold, benzene; moderately freely in hot, nearly insoluble in cold, alcohol, ether, and light petroleum. It parts with its sulphur to the same reagents, and with the same readiness as the naphthyl derivatives.

ab-Carboxyethylparahydroxyphenylthiocarbamide,
 $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_4 \cdot OH$.

Three grams of paramidophenol, dissolved in alcohol, were added to an equivalent proportion of the thiocarbimide; heat was evolved as before, and, on concentrating the mixture, 5 grams of product, in the form of fine, oblique, rhombic prisms were obtained, melting at $198.5-199^\circ$, after recrystallisation from alcohol.

0.2528 gave 0.2492 $BaSO_4$. $S = 13.54$.

$C_{10}H_{12}N_2O_3S$ requires $S = 13.34$ per cent.

Properties.—Moderately soluble in hot, nearly insoluble in cold, benzene; freely, but very slowly soluble in hot, moderately in cold alcohol; sparingly in ether, carbon bisulphide, and water. It is readily desulphurised by boiling with alkaline lead solution, slowly in the cold by neutral, and rapidly by ammoniacal silver nitrate.

FATTY DERIVATIVES.

ab-Carboxyethylmethylthiocarbamide, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_3$.

A quantity of the 33 per cent. aqueous solution representing 1.65 grams of methylamine, was freely diluted with alcohol, and cautiously added to 6.5 grams of the thiocarbimide, the vessel in which the experiment was conducted being immersed in running water. Very vigorous interaction ensued, with some fuming and liberation of a small quantity of sulphuretted hydrogen. On cooling, the liquid separated into two layers, the upper (toluene, benzene, and alcohol) containing some crystalline solid in suspension; whilst the lower layer of aqueous spirit held solid in solution. The suspended solid matter was removed by filtration, and the two liquids were separated and concentrated: in this way, three crops of crystals were obtained, and, since their respective melting points only varied within 2° , they were mixed and, after being purified by two recrystallisations from light petroleum, were obtained in the form of long prisms melting at $119-120^\circ$, without decomposition. Yield, 6.0 grams.

0.210 gave 0.3214 $BaSO_4$. S = 21.51. "

$C_5H_{11}N_2O_2S$ requires S = 21.64 per cent.

Properties.—Moderately freely soluble in hot and cold benzene, alcohol, ether, and chloroform; moderately freely in hot, sparingly in cold light petroleum; sparingly soluble in water. The alcoholic solution gives no precipitate with neutral silver nitrate, but becomes yellow, and parts with its sulphur on heating or on the addition of aqueous ammonia. Boiling with alkaline lead solution produces scarcely any change.

ab-Carboxyethylethylthiocarbamide, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_2H_5$.

Prepared in exactly the same manner as the preceding derivative, using 2.3 grams of ethylamine. The mixture separated into two layers as before, but no solid deposited until they were separated and concentrated, when a crop of fine, oblique prisms was obtained from the benzene-toluene portion of the mixture, and a few milligrams of solid in tufts of feathery needles from the aqueous spirit portion, in which small quantities of thiocyanic acid were detected, the crystals themselves, however, did not give the reactions of this substance,

and there was only 0.5° difference in melting point between the two crops. The product, purified by recrystallisation from light petroleum, melted at $79-80^\circ$ without decomposition. Yield 5.5 grams.

0.2218 gave 0.3184 BaSO_4 . $S = 19.73$.

$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_2\text{S}$ requires $S = 19.77$ per cent.

Properties.—Very freely soluble in hot and cold benzene, alcohol, ether, chloroform, carbon bisulphide, and acetone; moderately freely in hot and sparingly soluble in cold light petroleum. With desulphurising agents, it acts like the methyl derivative.

ab-Carboxyethylisobutylthiocarbamide, $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_4\text{H}_9$.

Combination between the amine (3.6 grams) and the thiocarbimide (6.5 grams) was effected as before, and was accompanied by marked evolution of heat. The product of the interaction separated as an oil, which, on separation from the mother liquor, slowly solidified, and, when purified by recrystallisation from light petroleum, was obtained in feathery tufts of needles, melting at $53-54^\circ$. Yield 7.5 grams.

0.202 gave 0.2314 BaSO_4 . $S = 15.74$.

$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ requires $S = 15.70$ per cent.

Properties.—Very freely soluble in all the ordinary solvents except light petroleum and water; in the former it is freely soluble when hot, and moderately freely in the cold, and it is slightly soluble in hot water. Its alcoholic solution darkens slowly on heating with neutral and rapidly with ammoniacal silver nitrate, whilst it desulphurises slowly on boiling with alkaline lead tartrate.

Action of Ammonia on Carboxyethylthiocarbimide.

Carboxyethylthiourea, $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{SH}$.—On treating 6.5 grams of the thiocarbimide with a slight excess of alcoholic ammonia an extremely energetic action occurred, accompanied by much fuming, evolution of heat, and the formation of small quantities of hydrogen sulphide. Solid matter separated at once, and 6 grams of product were obtained, and after being purified by recrystallisation from water, formed long prisms, melting at $139-140^\circ$.

0.2221 gave 0.3508 BaSO_4 . $S = 21.71$.

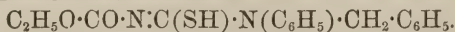
$\text{C}_4\text{H}_8\text{N}_2\text{O}_2\text{S}$ requires $S = 21.63$ per cent.

Properties.—Moderately soluble in hot, sparingly in cold benzene; freely soluble in hot, and nearly insoluble in cold alcohol and water; sparingly soluble in ether and carbon bisulphide. Its aqueous solution is readily desulphurised on heating with alkaline lead or

ammoniacal silver solutions, and with neutral silver nitrate affords a white precipitate, darkening slowly on heating.

Trisubstituted Thioureas.

Carboxyethylphenylbenzylthiourea,



—Only very slight evolution of heat occurred on mixing benzylaniline (in benzene solution) and the thiocarbimide in molecular proportion. No solid separated on concentration, but the addition of light petroleum precipitated a brown oil, which was dissolved in alcohol, and partly decolorised by treatment with animal charcoal, and, on concentrating after the removal of the latter by filtration, the solution slowly deposited crystals on standing; the product, purified by recrystallisation from light petroleum, 250 c.c. of this solvent being required for the solution of 3 grams of the solid, formed long needles, melting at 93—94°, with effervescence, to a clear greenish liquid.

0.2032 gave 0.156 BaSO₄. S = 10.5.

C₁₇H₁₈N₂O₂S requires S = 10.2 per cent.

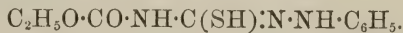
Properties.—Very freely soluble in all ordinary organic solvents except light petroleum, in which it is sparingly soluble when hot and almost insoluble in the cold; insoluble in water. Its alcoholic solution is not desulphurised by boiling with alkaline lead tartrate, but with neutral silver nitrate gives a white silver salt which does not darken appreciably on heating or on the addition of ammonia.

Carboxyethylpiperidylthiourea, C₂H₅O·CO·N:C(SH)·NH·C₅H₁₀. — Very vigorous action occurred on mixing 4.2 grams of piperidine with 6.5 grams of the thiocarbimide, and, after concentration to half its original bulk, the mixture, on cooling, became nearly solid, owing to the separation of a mass of fine interlacing needles; these were collected, washed with benzene, mixed with a second crop obtained from the mother liquor, and the whole (7 grams) recrystallised from light petroleum to a constant m. p., 99—99.5°.

0.2094 gave 0.2266 BaSO₄. S = 14.87.

C₉H₁₇N₂O₂S requires S = 14.805 per cent.

Properties.—Moderately freely soluble in hot and moderately in cold benzene; freely in alcohol, very freely in ether, and indefinitely soluble in chloroform; moderately freely in hot and sparingly in cold light petroleum. Its alcoholic solution is not desulphurised, or only very slowly, by alkaline lead tartrate; with neutral silver nitrate, no precipitate forms, but the liquid darkens slowly on heating; with the ammoniacal nitrate, a white precipitate is formed which blackens on heating.

*Phenylhydrazine and Carboxyethylthiocarbimide.**Carboxyethylphenylsemithiocarbazide,*

—The hydrazine was dissolved in alcohol, and, on adding it to an equivalent quantity of the thiocarbimide, interaction with evolution of heat and separation of solid matter took place at once. On cooling, the amount of solid increased considerably, and, when collected, washed with benzene, and recrystallised from alcohol, it was obtained as a mass of pure white needles, melting at 146.5° , and *remelting at the same temperature*.

0.2018 gave 0.2085 BaSO_4 . $\text{S} = 14.2$.

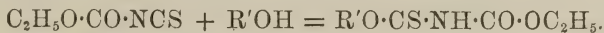
$\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}_2\text{S}$ requires $\text{S} = 14.28$ per cent.

Properties.—Moderately freely soluble in benzene, alcohol, and ether; moderately in hot and nearly insoluble in cold light petroleum. In alcoholic solution, it affords a white silver salt with neutral silver nitrate, blackening slowly on boiling.

Assuming that carboxyethylphenylsemithiocarbazide may be capable of existence in two stereoisomeric forms, the product obtained as above is probably the " β " modification, since, as noted, it remelts at the same temperature, and is also recovered unchanged in melting point after boiling its alcoholic solution with the addition of a few drops of strong hydrochloric acid. An attempt was therefore made, by keeping the mixture as cool as possible by running water, to produce the " α " modification; the product, however, proved to be the same as that already described; if, therefore, a second form is to be obtained, it would probably be necessary to work in a freezing mixture, but so far the writer has not conducted an experiment on these lines (see Marckwald, *Ber.*, 1892, **25**, 3098).

Ethereal Salts of Thiocarbamic acid.

Of these, five in all were prepared and are described below, the method of preparation consisting in adding the pure thiocarbimide, $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{NCS}$, to the corresponding alcohols, the amount of the latter used being in each case about double that required by the general equation



Interaction did not take place, as a rule, until the substances had been some three to five minutes in contact. In the case of the methyl derivative, when once the action commenced, the evolution of heat was so rapid that an appreciable quantity of the alcohol (MeOH) was volatilised; with benzyl alcohol, on the other hand, the mixed liquids

did not lose the smell of the thiocarbimide, nor was there any sensible evolution of heat until after about 20 minutes. The end product was obtained in each case by allowing the excess of alcohol to evaporate spontaneously, and the yields were practically quantitative.

Methylic Carboxyethylthiocarbamate, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OCH_3$.—Prepared from methylic alcohol and the thiocarbimide. Large, glistening prisms from mother liquor, and feathery tufts of needles melting at $65-66^\circ$, after recrystallisation from light petroleum.

0.2041 gave 0.2929 $BaSO_4$. $S = 19.72$.

$C_5H_9O_3NS$ requires $S = 19.65$ per cent.

Properties.—Very freely soluble in all ordinary solvents except water and light petroleum; it is insoluble in the former, and dissolves freely in the latter when hot, but only sparingly in the cold.

Ethylic Carboxyethylthiocarbamate (*Carboxyethyl- β -thiourethane*), $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_2H_5$.—Was obtained from the thiocarbimide and corresponding alcohol in rosettes of yellowish needles, melting at $44-45^\circ$.

0.2029 gave 0.2699 $BaSO_4$. $S = 18.28$.

$C_6H_{11}O_3NS$ requires $S = 18.21$ per cent.

The chief difference between this and the preceding compound, in respect to its behaviour to solvents, consists in its being slightly soluble in water, and more freely soluble in warm, light petroleum, the latter solution remaining persistently supersaturated on cooling.

Propylic Carboxyethylthiocarbamate, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_3H_7$.—From the thiocarbimide and normal propyl alcohol. Long, thick, yellow prisms, melting at $31-32^\circ$, and so freely soluble in all ordinary solvents that recrystallisation could only be effected with difficulty.

0.221 gave 0.2684 $BaSO_4$. $S = 16.69$.

$C_7H_{13}O_3NS$ requires $S = 16.77$ per cent.

Isobutylic Carboxyethylthiocarbamate, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OC_4H_9$.—This substance was obtained as a pale, greenish-yellow liquid, readily miscible with all solvents except water; it did not solidify at -8° . It was analysed after standing for a month over strong sulphuric acid, excess of the alcohol having first been expelled.

0.2368 gave 0.272 $BaSO_4$. $S = 15.74$.

$C_8H_{15}O_3NS$ requires $S = 15.62$ per cent.

Benzylic Carboxyethylthiocarbamate, $C_2H_5O \cdot CO \cdot NH \cdot CS \cdot OCH_2 \cdot C_6H_5$.—In this case, as soon as the action was complete, the contents of the vessel in which the experiment was made became nearly solid through the separation of a mass of yellowish, interlacing needles;

by recrystallisation from light petroleum, the product was obtained in tufts of white needles, melting at 66—67°.

0.2003 gave 0.1974 BaSO₄. S = 13.54.

C₁₁H₁₃O₃NS requires S = 13.406 per cent.

It is moderately freely soluble in benzene and alcohol, very freely in chloroform, moderately freely in hot, and nearly insoluble in cold, light petroleum.

In respect to their behaviour with the usual reagents for the removal of sulphur, the above five compounds resemble each other more or less closely; with neutral and ammoniacal silver nitrate they yield white silver salts, the former precipitates darkening slowly on heating, while complete desulphurisation is readily effected on heating the latter. Only very slight darkening occurs on boiling their alcoholic solutions with alkaline lead tartrate, but, if the solid is first dissolved in warm, dilute potash solution, and lead nitrate be added, marked desulphurisation occurs on heating.

Carboxyethylthiocarbimide.

That this was obtained pure has been mentioned when dealing with its phenyl derivative, and the fact that it was used in the preparation of the thiocarbamates leads the writer to insert here a brief description of its isolation and properties.

A quantity of the benzene-toluene solution, representing 15 grams of the thiocarbimide, was divided into three equal parts and treated as follows.

I. *Distilled at Atmospheric Pressure.*—All the solvents came over below 140°; the temperature then rose rapidly to 180°, when a small quantity of the thiocarbimide was obtained; but there was obvious, though not very marked, decomposition, the residue left in distilling flask darkening in colour and becoming sticky.

II. *Steam Distilled.*—Solvents came over very rapidly at first, then the thiocarbimide itself, but, at the moment when it commenced to distil, there was considerable fuming, sulphuretted hydrogen was detected both by its odour and action on lead paper, and the process was therefore stopped.

III. *Distilled under Diminished Pressure.*—Benzene and toluene were expelled before 60° was reached, and, on changing the receiver, 2.5 grams of a colourless, highly refracting liquid, boiling at 66—67° under a pressure of 21 mm., were obtained. It afforded the following data on analysis.

0.205 gave 0.3648 BaSO₄. S = 24.46.

0.1894 „ 18 c.c. moist nitrogen at 18° and 749 mm. N = 10.81.

C₄H₅O₂NS requires N = 10.71; S = 24.45 per cent.

The formula of this substance having been established already by the complete analysis of its phenyl derivative, it was not considered necessary to analyse it further. The weight of the pure thiocarbimide, obtained by distillation in a vacuum, indicates a yield of only 50 per cent.; but, apart from the evidence of an almost quantitative yield afforded by the amounts of some of the derivatives already described, on passing ammonia through the distillate which came over below 60*, and thus converting the thiocarbimide into carboxyethylthiourea, it has been found that the original yield must have been practically theoretical.

Properties.—Carboxyethylthiocarbimide is freely miscible with benzene, toluene, ether, and light petroleum; it is apparently very slightly soluble in, and is only very slowly decomposed by, water at the ordinary temperature, as is shown by an experiment described below, and that a much higher temperature does not greatly increase the rate of decomposition is evident from the fact that a small quantity of it was obtained almost pure by steam distillation. It is desulphurised at once, and in the cold, by alkaline solution of lead and by ammoniacal silver nitrate. These latter facts, coupled with the series of derivatives it has afforded, and the results of the experiment now to be described, serve to establish its claim to be a true thiocarbimide.

Action of Water.—About 0.2 gram of the thiocarbimide was added to 25 c.c. of water, the mixture was shaken vigorously, and, when the oily droplets had subsided, a portion of the clear aqueous layer gave only a scarcely perceptible reaction for thiocyanic acid on treatment with ferric chloride. This test was constantly repeated during a period of over a month, and at no time was there any marked thiocyanic reaction, though evidence of decomposition, resulting in the evolution of sufficient sulphuretted hydrogen to be detected by its odour and the usual tests, was noticed the day after the mixture was made. After six weeks, the oily droplets of the thiocarbimide had disappeared, a small quantity of brownish semi-crystalline matter had separated, and the liquid, which had some time previously lost all odour of either sulphuretted hydrogen or the thiocarbimide, still reacted very faintly for thiocyanic acid, but *contained something which gave an appreciable precipitate of silver sulphide* on treatment with ammoniacal silver nitrate.

Another experiment was tried, boiling a few drops of the thiocarbimide with water, cooling rapidly, and adding ferric chloride, and, in this case also, only a faint reaction for thiocyanic acid was obtained; but if it be first treated with potash solution, neutralised

* That is, the solvents which came over below 60°, under a pressure of 21 mm., carrying some of the thiocarbimide with them.

with hydrochloric acid, and ferric chloride added, a well marked thiocyanic reaction is obtained. In respect to the result mentioned above (in italics), it may be here pointed out that, in the course of the joint investigation (Trans., 1895, **67**, 572), to which reference has already been made, a somewhat similar result was obtained by the action of water on succinyldithiocarbimide, $C_2H_4(CO \cdot NCS)_2$, save that in this case well marked reactions for succinic and thiocyanic acids were obtained, in addition to the evidence of the presence of something capable of parting with its sulphur to silver nitrate.

At no time during the experiment just described was the amount of thiocyanic acid present sufficient to be estimated, unless, perhaps, colorimetrically, and it seems that almost the only possible explanation to be given of the presence in the aqueous solution (after the thiocarbimide, $EtO \cdot CO \cdot NCS$, had disappeared) of a substance capable of giving up its sulphur to ammoniacal silver nitrate, is to be found in the slow formation of hydrogen thiocarbimide, $HNCS$, itself, the latter substance also slowly passing into the more stable thiocyanic acid. This explanation is, however, advanced with all due reserve in view of the probably highly unstable nature of the combination $H \cdot N : C : S$, and the necessity for repeating the experiment with quantities sufficiently large to permit of the examination of all the products of the decomposition, and in particular of the brown semi-crystalline solid which separated during its course.

Constitution of Nitrogen Bases and Isomerism.

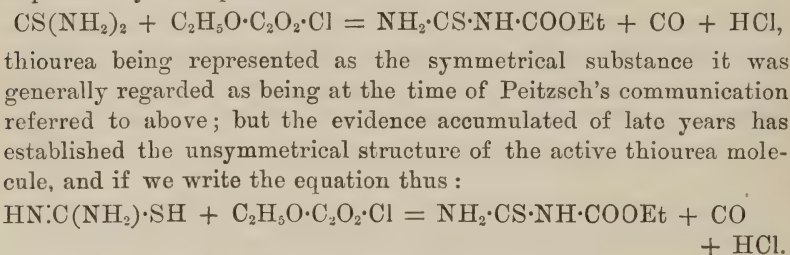
In respect to the constitution of the various derivatives of carboxyethylthiocarbimide described in this communication, the symmetrical form, $CS < \begin{smallmatrix} NHR \\ NHR' \end{smallmatrix}$, has been provisionally given to the products obtained by effecting interaction between the substance in question and primary amines; while the derivatives resulting from its combination with ammonia and secondary amines, are regarded as conforming to the unsymmetrical formula usually assigned to "thiourea" itself, $HN : C < \begin{smallmatrix} NH_2 \\ SH \end{smallmatrix}$, and are called "thioureas," as suggested by Reynolds (see Trans., 1891, **59**, 395). Thus, the trisubstituted derivative obtained by interaction with benzylaniline becomes carboxyethylphenylbenzylthiourea, $EtO \cdot CO \cdot N : C < \begin{smallmatrix} NPh \cdot C_7H_7 \\ SH \end{smallmatrix}$, or, if the nomenclature recently suggested (Dixon, Trans., 1895, **67**, 564) be adopted, it becomes *n*-carboxyethyl-*ν*-phenylbenzylthiourea. That the substance in question and the derivatives obtained by the interaction of carboxyethylthiocarbimide with ammonia and with piperidine have not their sulphur attachments occupied by a radicle is shown by the

fact that they do not yield any traces of alkyl sulphide or hydro-sulphide on treatment with caustic alkali. Further than the above brief note the author does not intend dealing with the constitution of these derivatives until they have been studied in detail, for which purpose several of them have been prepared in quantity; he would now desire to turn to two cases of isomerism which it is necessary to deal with at length.

Carboxyethylthiourea, $\text{EtO}\cdot\text{CO}\cdot\text{CSN}_2\text{H}_3$, and carboxyethylphenylthiocarbamide, $\text{EtO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, are isomeric with the so-called ethylic isothioallophanate and ethylic isophenylthioallophanate respectively.

Taking them in the order given, ethylic isothioallophanate is formed, according to Peitzsch (*Ber.*, 1874, **7**, 896), by the action of ethoxalyl chloride on thiourea; but the paper in which this result is set forth is very brief, no analytical or other data of importance are given, the author stating, however, that the work would be taken up again; but the writer has not been able to find any further reference to it.

In the latest addition of Beilstein's *Handbuch*, the interaction is explained by the equation:



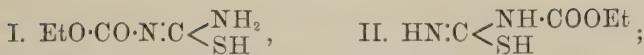
it at once becomes apparent that this explanation of the interaction is based on the assumption that ethoxalyl chloride is capable of converting the unsymmetrical thiourea molecule into the symmetrical or "thiocarbamide" form in a derivative—a result scarcely possible.

In *Ber.*, 1888, **21**, 402, Pawlewski claims to have obtained the hydrochloride of Peitzsch's compound, $\text{C}_4\text{H}_8\text{N}_2\text{SO}_2\cdot\text{HCl}$, in rhombic prisms melting at 117° , by the action of ethylic chlorocarbonate on thiourea. It became of interest, therefore, to ascertain, if possible, first, if the formula assigned to this compound by Peitzsch was correct, and, secondly, its relationship to carboxyethylthiourea,

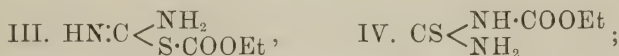


obtained by the writer by the direct action of ammonia on carboxyethylthiocarbimide.

Of four possible isomeric forms in which this compound could exist, two are unsymmetrical and have their sulphur directly attached to carbon, thus—

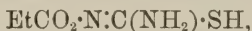


one (III) is unsymmetrical, and of the pseudothiourea type, with sulphur in direct union with the alkyl group—



whilst the fourth (IV) is the symmetrical formula assigned to “ethylic isothioallophanate.”

Assuming that carboxyethylthiourea is not tautomeric, and that its structure is in accordance with the unsymmetrical formula usually given to substituted thioureas, only one or other of the first two formulæ could be given to it, since it apparently undergoes no change on boiling with strong alkali, and of these the first,



is taken as probably better representing the thiourea structure. This reduces the choice of a formula for Peitzsch's compound to the symmetrical one attributed to it, or to that of a pseudothiourea; the method of preparing it alone indicates that the former can scarcely be correct, and we thus, by a process of exclusion, arrive at the latter as the only one left for this compound, and experimental evidence is not lacking in support of this deduction.

Some time ago Professor A. E. Dixon commenced an examination of the reactions by which “ethylic isothioallophanate” and similar compounds were obtained, and, in reference to the work of Peitzsch and Pawlewski, has kindly given me the following note.

Note on the “Ethylic Isothioallophanate.”

“Pawlewski, in a brief note (*Ber.*, **21**, 402) records that chlorocarbonic ether acts instantly on sulphourea, forming a compound, $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CO} \cdot \text{OC}_2\text{H}_5, \text{HCl}$, which melts at 117° , and contains 19.29 and 19.23 per cent. of chlorine, against 19.24 calculated. This substance is probably the hydrochloride of Peitzsch's compound (*Ber.*, **7**, 896), the reaction, however, occurring differently from that observed by Peitzsch.

“The constitution assigned to the above substance does not accord very satisfactorily, either with the method whereby it is produced or with its properties, so far as they are recorded; a few experiments were, therefore, some time ago commenced on this and certain allied compounds, with results which tended to confirm the doubt as to its structure. Further study of the derivative from thiourea and ethylic chlorocarbonate was deferred on account of other work, but a recent direct synthesis by Mr. Doran, from ammonia and carboxyethylthiocarbimide, of a substance possessing

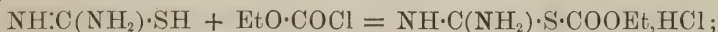
totally different properties, having practically excluded the formula hitherto accepted for Pawlewski's compound, the examination of the latter was resumed.

"Union occurred very vigorously, with evolution of much heat, on gently warming the constituents together, and a slightly moist, white solid was formed which, after well pressing in bibulous paper, shrank at about 90° , and effervesced at $98-99^{\circ}$; it smelt unpleasantly, and appeared to be somewhat deliquescent. It was freely soluble in water, alcohol, acetone, and ethylic acetate, practically insoluble in carbon bisulphide, chloroform, and benzene; from the alcoholic solution it was precipitated by the two latter as a pasty solid. The aqueous solution had an acid reaction, and gave with neutral silver nitrate a precipitate of silver chloride; the solid, moreover, effervesced when treated with sulphuric acid, evolving fumes of hydrogen chloride.

"Ammoniacal silver nitrate produces a bright yellow, silver compound which rapidly blackens, especially if much ammonia be present; using alcoholic solutions, the yellow precipitate appears to be more stable, but was, under these conditions, soon decomposed, yielding metallic sulphide. Cold dilute caustic alkali when added to the aqueous hydrochloride, turns it somewhat brownish, and an intolerable odour of mercaptan or ethylic sulphide is produced; if to this solution a lead salt be added, a bright yellow precipitate forms, which gradually decomposes into lead sulphide; this change occurs at once on warming. If the dilute aqueous solution is mixed with lead nitrate and caustic potash gradually dropped in, a white precipitate is formed, redissolving at first, and then becoming permanent; next it turns yellow, and, finally, when excess of potash is present, it blackens—all in the cold. Mixed similarly with solution of mercury, and then treated with excess of alkali, a yellow precipitate results, quickly changing to black, (HgS). With cadmium chloride, in like manner, a white precipitate, changing to yellow, is obtained, and with bismuth nitrate (which gives a clear, lemon-yellow colour with the hydrochloride) a yellowish-brown precipitate, soon decomposing into bismuth sulphide. In all these cases, also, the sulphuretted odour, especially on warming, is very marked and disagreeable; the escaping gases turn lead paper yellow.

"The saline nature of this chlorocarbonate derivative, together with the ready liberation of volatile compounds of sulphur on mere addition of cold alkali, and the behaviour with metallic salts (in presence of alkali) above mentioned, all point in the strongest manner to the view that sulphur, and not nitrogen, is engaged with the atomic complex introduced by the chlorocarbonate, and hence that the compound is constituted similarly to the basic and evil-smelling sub-

stances obtained by the action of alkalis on the addition products of thiourea and the alkylogens. Accordingly the interaction may be explained as follows.

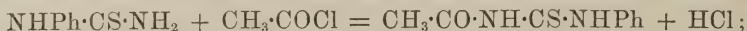


the resultant compound being the hydrochloride of carboxyethyl- ψ -thiourea. By hydrolysis with potash this can afford the corresponding salt of ethyl- α -thiocarbonic acid, $\text{EtO}\cdot\text{CO}\cdot\text{SH}$, a substance which easily decomposes (Bender, *Annalen*, 1868, **148**, 137) into hydrogen sulphide, mercaptan, &c."

Turning now to the second supposed case of isomerism, *ab*-carboxyethylphenylthiocarbamide, $\text{EtO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, and "ethylic isophenylthioallophanate," $(\text{NH}_2\cdot\text{CS}\cdot\text{NPh}\cdot\text{COOEt})$; in a communication "On the Action of Ethylic Chlorocarbonate on Phenyl- and di-Phenylthioureas," in *J. pr. Chem.*, 1885, **32**, 261, *et seq.*, Seidel describes an experiment whereby, as the result of interaction between ethylic chlorocarbonate and phenylthiocarbamide, "carboxyethylthiourea or, as it is termed in Beilstein's *Handbuch*, "ethylic phenylthioallophanate," was produced. In carrying out his experiment, the author used an excess of the chlorocarbonate; he notes the evolution of carbon dioxide, hydrogen chloride, and ethylic chloride during the course of the action, and states that the end product was a yellow oily mass which crystallised slowly in a desiccator; after six months it partly solidified, and, as the oil was not removable, the crystals could not be purified for analysis. Attempts to wash with hot absolute alcohol and benzene decomposed the solid, the mass regenerating phenylthiourea. He further states that the compound was "too unstable for its constitution to be determined," and referring to Miquel's preparation of acetylphenylthiocarbamide (*Ann. Chim. Phys.*, 1877, **11**, 318) from acetylthiocarbimide and aniline, assumes that his "carboxyethylphenylthiourea," or "ethylic phenylthioallophanate," is a similarly constituted symmetrical compound, having the formula $\text{COOEt}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$; as evidence of its structure, he states that on heating at 50—60°, with an excess of acetyl chloride, using a reflux condenser, this substance yields acetylphenylthiocarbamide, saying that this shows that the "negative," COOEt group is expelled by $\text{CO}\cdot\text{CH}_3$.

There is considerable difficulty in reconciling the properties of this substance with those of a di-substituted thiourea; moreover, the tri-substituted compound, ethylic diphenylthioallophanate, also obtained by Seidel (*loc. cit.*, 262, *et seq.*) by the action of ethylic chlorocarbonate on thiocarbanilide, does not exhibit such extreme instability—distinctly the opposite, in fact, as its recorded reactions indicate. With regard to the formation of acetylphenylthiocarbamide by the

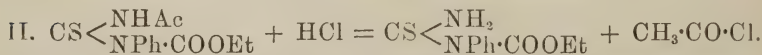
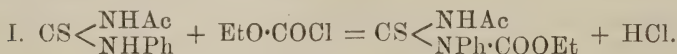
action of acetyl chloride on Seidel's compound, it seems reasonably certain that this is due solely to the readiness with which the compound in question regenerates phenylthiocarbamide, leaving the latter free to interact with the chloride in accordance with the equation,



whilst, as further proof of the untenable nature of the evidence adduced in support of the constitution assigned to "carboxyethylthiourea," the writer will show later that the group COOEt is *positive* to $\text{CH}_3\cdot\text{CO}$.

The writer has, so far, only been able to verify the marked instability of the product of the interaction between ethylic chlorocarbonate and phenylthiocarbamide, and these appear to be only two possible explanations for it; the first is that the interaction results in the formation of the hydrochloride of a ψ -thiourea in the manner already described when dealing with Peitzsch's "ethylic thioallophanate" (*q.v.*); whilst the second is based on the assumption that the two interacting substances, $\text{EtO}\cdot\text{COCl}$ and $\text{CSN}_2\text{H}_3\text{Ph}$, can combine to form an unstable molecular compound analogous to the substance obtained by Claus (*Ber.*, 1875, 8, 42) by the action of acetyl chloride, on thiourea itself—a compound which decomposes without the formation of an acetylated thiourea if treated with hot alcohol; owing to the extreme instability of the product, the latter explanation is regarded as being more probably correct.

To consider now the so-called "ethylic isophenylthioallophanate," or "carboxyethylisophenylthiourea," $\text{NH}_2\cdot\text{CS}\cdot\text{NPh}\cdot\text{COOEt}$: Seidel (*loc. cit.*, 274) obtained it, as a result of interaction between ethylic chlorocarbonate and acetylphenylthiocarbamide; the experiment was made with a view to obtain a tri-substituted thiourea, and the author states, in referring to the final product, "strange to say, the isomer (*i.e.*, of his 'carboxyethylthiourea') was obtained," and proceeds to explain its formation, on the assumption that carboxyethylacetylphenylthiourea was formed during the course of the action, by the following equations.



Mere inspection of the above equations reveals the fact that the explanation given is scarcely tenable, in so far as it assumes a highly improbable quasi-migration of the phenyl group from one part of the molecule to another, but the author's reasons for advancing it are self-evident; having already concluded that the very unstable compound resulting from the action of ethylic chlorocarbonate on phenyl-

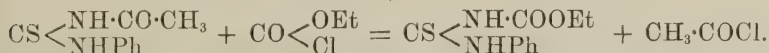
thiocarbamide was "carboxyethylphenylthiourea," and that the action of acetyl chloride on this substance to afford acetylphenylthiocarbamide, was proof of the "negative" character of the COOEt-group, the above given explanation was the only consistent one left to him. In view of the fact that "ethylic isophenylthioallophanate," in its solubility relations, crystalline form, and general characteristics, so far as they are described, appeared to be identical with the writer's carboxyethylphenylthiocarbamide, while there is only 3° difference in the melting points of the two substances, namely 127° (uncor.) for the first named, and 130° (uncor.) for the second, it became necessary to repeat his experiment, and this was done with the following results.

A mixture of 4 grams of finely powdered, well dried acetylphenylthiocarbamide, and 5 grams of ethylic chlorocarbonate, was heated on the water bath in a reflux apparatus; interaction, accompanied by the evolution of acetyl chloride and hydrogen chloride, commenced before the boiling point was reached and complete dissolution of the solid was effected after about 15 minutes heating; a yellowish-brown liquid of faint sulphuretted odour, was formed, which, on cooling, became almost solid, through separation of crystalline matter. The crystals, freed as completely as possible from adherent mother-liquor by pressing between folds of bibulous paper and purified by two recrystallisations from alcohol, were obtained in the form of pure white, apparently monoclinic tables, melting at 129—130°.

0.2074 gave 0.2196 BaSO₄, or S = 14.55.

CS(NH)₂Ph·COOEt requires 14.30 per cent.

The substance obtained in this way was in every respect identical with the carboxyethylphenylthiocarbamide produced synthetically from carboxyethylthiocarbimide and aniline. The interaction may therefore be formulated as follows.



An experiment was now made to test the validity of the statement concerning the "negative" character of the COOEt-group, though, when the result just detailed is considered, it seemed scarcely necessary. The above named thiocarbamide was selected and 2 grams of it was heated, using a reflux condenser, for half-an-hour with a large excess (5 grams) of acetyl chloride,—the latter being kept in brisk ebullition; no sign of interaction was observed during the experiment, and, eventually, 1.9 grams of unchanged thiocarbamide was recovered; therefore, it may reasonably be concluded that, in so far at least as acetyl chloride and a thiocarbamide of the type dealt with are concerned, the group CO·OEt is positive to CH₃·CO.

The results arrived at in the preceding paragraphs dealing with the supposed cases of isomerism may be briefly summarised by the statement, that the "ethylic thioallophanate" of Peitzsch and Pawlewski, the "carboxyethylphenylthiourea," or "ethylic phenylthioallophanate," and "ethylic isphenylthioallophanate" of Seidel are substances which apparently do not exist at present; the first-named appears to be a pseudo-thiourea, or its hydrochloride; the second, an unstable molecular compound of ethylic chlorocarbonate and phenylthiocarbamide; whilst the third is identical with the symmetrical carboxyethylphenylthiocarbamide described in this communication.

In conclusion, the author wishes to acknowledge his indebtedness to Professor Dixon for much valuable suggestive help during the course of the work described, and to state that he hopes shortly to lay before the Society an account of carboxymethylthiocarbimide, a few derivatives of which have already been obtained, and that he purposes extending this research to some of the other chlorocarbonates, and to methoxalyl and ethoxalyl chlorides.

*Chemical Department,
Queen's College, Cork.*

XXXIV.—*Connection between the Atomic Weight of Contained Metals, and the Crystallographical Characters of Isomorphous Salts. The Volume and Optical Relationships of the Potassium, Rubidium, and Cesium Salts of the Monoclinic Series of Double Sulphates, $R_2M(SO_4)_2 \cdot 6H_2O$.*

By ALFRED E. TUTTON, ASSOC. R.C.S.

IN a previous communication (Trans., 1893, **63**, 337), the results of a detailed investigation of the morphological characters of 22 double sulphates of this series were laid before the Society. The present memoir deals with the volumes and the optical properties of these same 22 salts, and thus completes their crystallographical history. The interesting nature of the morphological relationships described in the former communication rendered it very desirable that an investigation, of as thorough a nature, should be carried out concerning the physical properties of the salts. This series of isomorphous salts is undoubtedly the most important yet known to us among those crystallising in the systems of lesser symmetry, and no effort has been spared to render the work now presented as complete

and accurate as possible. Each salt has been studied in the same detailed manner as the normal sulphates of potassium, rubidium, and caesium described to the Society in 1894 (*Trans.*, 1894, **65**, 628), and results of equal interest to those resulting from the latter investigation have followed.

The data hitherto existing concerning these salts have been of a character totally inadequate for the purposes of making important deductions concerning their relationships. The potassium salts of the series were studied in the year 1859 by Murnann and Rotter (*Sitz. Ber. der Kais. Akad. Wiss.*, **34**, 135), but the character of the work can only now be regarded as affording very rough approximations as regards the optic axial angles of the salts, and as very crude indeed with respect to the refractive indices, the β indices alone being usually determined, and in several cases the rough results given will be shown to be very inaccurate. Two of the potassium salts, those containing magnesium and iron, were included by Topsøe and Christiansen in their well-known investigation in 1874 (*Ann. Chim. Phys.*, 1874, [5], **1**, 1), but even in this work the optic axial angles are only given for sodium light, and the β refractive indices alone were directly determined; the indirectly determined α and γ indices will be shown to deviate considerably from the values now given, all of which were directly determined. The most important work which has hitherto been carried out on this series is that of Perrot (*Archiv. des Sciences phys. et nat. Genève*, 1891, 26, and 669, and 1893, 3), who has investigated the eight rubidium salts, and the potassium and caesium salts containing zinc as the second metal. The refractive indices of these salts were determined by Perrot by means of Soret's total-reflection method, thus avoiding the necessity of grinding prisms, and it is very satisfactory to find that the values of the indices thus determined, evidently with great care, coincide almost exactly with the values now given for the same salts, as determined by means of accurately orientated prisms. Perrot has not determined the other optical properties with sufficient completeness. The optic axial angles were usually determined indirectly, with the introduction of the intermediate index of refraction of the crystal in the calculation, a method open to considerable error, and usually only for sodium light. The error in the stauroscopic determinations of the orientation of the axes of the optical ellipsoid is also larger than in the determinations now given. The densities, moreover, were determined by means of the hydrostatic balance, and frequently differ considerably from the numbers now presented, determined with much larger quantities of the salts by a pycnometer method conducted with extreme precautions. The point of Perrot's work was the refraction observations, as exemplifying the utility of Soret's method, and the accord between

those observations and the work now published is all that could be desired.

Seven of the eight caesium salts have never hitherto been subjected to investigation.

From the foregoing statement of previous work on the series, it will be evident that an exhaustive investigation of the whole 22 salts, of a most careful character, and on strictly comparable lines, was very desirable in order that our knowledge of this important series might be sufficiently accurate to enable general deductions of a trustworthy nature to be drawn as to the effect of the replacement of one metallic constituent by another.

METHOD OF WORK.

Volume Investigation.

The Densities.—The method adopted for determining the relative densities was the “pycnometer method with cap,” fully described in the communication concerning the simple normal sulphates (*loc. cit.*, 650), and due to Chapman Jones. The determinations were in every case conducted with the most transparent crystals, ground to the finest powder in an agate mortar, and sifted through fine platinum gauze. Except in those cases requiring special treatment, owing to efflorescence, which will be described in connection with the particular salts concerned, the powder was dried for a short time at the ordinary temperature between hard-pressed filtering paper, free from fluff, and then resifted several times, in order to remove the small quantity of moisture due to the minute inclusions of mother liquor. When it no longer adhered to a glass rod it was transferred to the pycnometer, and the determination proceeded with. Carbon tetrachloride was employed throughout as the liquid, and its specific gravity was frequently verified during the determinations. Considerable quantities, from 2 to 5 grams, of the salts were employed in each determination, and they were taken from different crops, belonging to two distinct preparations. Four determinations were made for each salt. The rubidium and caesium sulphates employed in the preparations were largely derived from the stock obtained at the commencement of this work, analyses of which were given in the communication concerning the morphology of the series (p. 340); it was found necessary to supplement it, however, by an additional quantity supplied by Merck, of the same high order of purity as the last, and analyses and spectroscopic examination of which yielded equally satisfactory results.

All the densities were determined at 20°, and the results are compared with water at 4°. Hence they are all strictly comparable.

Distance Ratios (Topic Axes of Muthmann).—The formulæ employed in calculating these ratios are those referred to in the memoir concerning the simple alkaline sulphates (p. 658), as having been suggested to the author by Professor Becke, of Prague, immediately after the appearance of the memoir concerning the morphology of the double sulphates; they are Muthmann's more recent topic axes for rhombic symmetry, modified for monoclinic symmetry by the introduction of the sine of the monoclinic axial angle β . The actual meaning of the three ratios, χ , ψ , and w , is, that they represent the relative distances apart of the centres of the structural units, or groups of units if the structure consists of more than one kind of unit together corresponding to the constitutional formula, along the directions of the three morphological axes. The formulæ are as follows.

$$\chi = \sqrt[3]{\frac{a^2V}{c \sin \beta}}; \psi = \sqrt[3]{\frac{V}{ac \sin \beta}}; w = \sqrt[3]{\frac{c^2V}{a \sin \beta}}.$$

where V is the molecular volume, and a , b , and c are the ordinary morphological axial ratios.

Optical Investigation.

The optical investigation of a large number of salts of a low order of symmetry, in accordance with the exhaustive scheme contemplated, involving the preparation of some hundreds of accurately orientated section-plates and prisms and their examination in monochromatic light, was a task of some magnitude, and it was the recognition of this fact which led the author to devise and cause to be constructed the instrument for grinding accurately orientated section-plates and prisms, and the monochromatic illuminator, which were described to the Royal Society two years ago (*Phil. Trans.*, 1894, A, 887 and 913). Without the former instrument, it is doubtful whether this work would ever have been completed, it would certainly never have been endowed with the same accuracy. About 200 section-plates have been prepared by means of it during the progress of this work, at least two for each salt parallel to the symmetry plane for use in the determination of the directions of the principal planes of the optical ellipsoid, three perpendicular to the first median line of the optic axes for the determinations of $2E$, the apparent optic axial angle in air, and $2Ha$, the apparent acute angle in an immersion liquid, and three perpendicular to the second median line for the measurement of $2Ho$, the apparent obtuse angle in the immersion liquid. In all cases, the highest accuracy of orientation was ascertained to have been attained, although frequently a complicated matter owing to awkward relations between the morphological faces and the direc-

tions of the median lines, due to the monoclinic nature of the symmetry. The plates perpendicular to the first median lines invariably exhibited the interference figures symmetrical to the centre of the field of the polariscope. For the determinations of refractive index about $150\ 60^\circ$ prisms, at least six from each salt, were also ground, each of which was formed by two faces symmetrically arranged, that is, equally inclined, to one of the principal planes of the optical ellipsoid, and whose intersecting edge was parallel to one of the three axes of the ellipsoid. Hence each prism directly furnished two of the three refractive indices. Usually two such prisms, in complementary directions, were ground upon the same crystal, the pair of prisms thus furnishing all three indices, and one of them in duplicate. This is probably the first time that this has been achieved, certainly on such a scale, with crystals of symmetry as low as monoclinic. The new grinding instrument has thus proved invaluable, and has more than fulfilled all that was expected of it. Moreover, barely half a dozen crystals among so large a number have been broken during the grinding, and the labour spent on them lost.

The section-plates and prisms were employed whenever possible without cemented cover glasses; the polish furnished by the two polishing discs of the instrument, of very finely ground glass and of polished glass respectively, lubricated with brick oil, has in many cases been ample to permit of excellent observations being obtained with them directly. In the cases of the strongly coloured, and hence absorbent nickel and cobalt salts, the rapidly efflorescing cadmium salts, and occasionally, owing to special difficulties, with some of the crystals of the copper salts, it has been necessary to employ thin miniature cover glasses, cemented with a solution of hard balsam in benzene. The large number of observations taken, however, will have eliminated any slight error due to the cover glasses, and in cases where there has been any doubt the cover glasses have been removed, re-set, and the observations repeated.

All the observations of optic axial angle and refractive index have been carried out for several wave-lengths, five in the case of the former and six in the case of the latter. The new monochromatic illuminator has been employed throughout, the source of light being the lime-light, in order that the receiving and exit slits might be as fine as possible and the monochromatism of a high order. The saving of time and the convenience generally afforded by this instrument has been immense, and the powerful illumination given by it has been a very great aid to accuracy in the cases of the highly coloured salts, an ordinary lithium flame, for instance, being almost incapable of penetrating a thick plate or a prism of any of the green salts containing nickel as the second metal, whereas with the monochromatic illumi-

nator a comparatively bright interference figure or image of the spectrometer slit is afforded.

Wülfing (*Min. und Petrogr. Mitth.*, 1895, 15, 49) has since described a somewhat similar spectroscopic monochromatic illuminator, of cheaper construction, and criticises the author's use of a ground glass screen to diffuse the light sufficiently to fill the field of the observing instrument, on account of its weakening of the light. Instead, he arranges the observing instrument, the polariscopical goniometer, at such a distance from the exit slit that the bundle of rays, emerging from the latter, when it reaches the objective of the polariscope has attained the same diameter as that objective; he then introduces a lens whose focal length is equal to the distance from the slit, and thus fills the objective with parallel rays. The author of the present communication, long ago, before the instrument was described to the Royal Society, tried this method of diffusion, but discarded it for the ground glass diffuser, for the reason that although the illumination was slightly superior it was by no means so satisfactory. For unless the eye was maintained exactly in one position in front of the polariscope, it was found that the illumination became uneven, and dark patches were seen at the sides, very disturbing during the observation of interference figures, and the illumination even disappeared altogether. Doubtless a cap with a small central hole in front of the analyser might obviate this, but the evenness of the field is so perfect when ground glass is employed, and remains so, however much the eye moves about, that the author prefers it infinitely, since it renders the whole aperture of the nicol available, and the interference figures clear and constant. As regards the weakening of the intensity of the light, that depends largely on the texture of the glass diffuser.

As stated in the memoir (*loc. cit.*), describing the monochromatic illuminator, two screens are used. One is so finely ground that objects behind it can be seen, slightly blurred, through it; this is used for refractive index work with the Fuess spectrometers, Nos. 1a and 2a, and gives beautifully even images of the Websky slit. The other is only slightly coarser, being of the texture of the finest camera focussing screens; this is employed for optic axial angle work with the polariscopical goniometer, and the diffusion is just sufficient, and no more than is required, to fill the field of the polariscope. The intensity of the illumination is very little less than when the lens is employed, and this is not noticed when the lime-light or an electric arc is available, one or other of which the author always employs in work of the character of the present investigation, in order to be able to use slits of very fine opening, so as to obtain very nearly perfect monochromatism. The whole apparatus has worked admir-

ably during the course of this work, and in the cases of salts exhibiting extraordinary interference phenomena, such as the beautiful example of caesium magnesium sulphate, to be described in the course of this communication, and that of rubidium sulphate, previously described, it has proved simply invaluable.

Orientation of Axes of Optical Ellipsoid.—The determinations of the extinction angles in the symmetry plane were made with a new Fuess stauroscope fitted with a Calderon double calcite plate. The extinctions could in most cases be determined to $5'$. The sections parallel to the symmetry plane were always made from well-developed crystals, so that the portions of the faces left on the edges of the section afforded good images of the goniometer signal. The basal plane face $c(001)$ was usually taken as reference face in determining the position of the section when cemented upon one of the rectangular glass plates given with the Fuess instrument, and the crystal was arranged so that this face was as nearly as possible parallel to the marked reflecting edge of the glass plate. The small correction angle was measured on the excellent goniometer of the grinding instrument as soon as the cementing film of balsam solution had sufficiently set. Observations were made with the crystal above the plate, and then with the plate inverted and the crystal below it, in order to eliminate the error of coincidence between the direction of the nicols and the zero graduation of the circle. The dispersion of the median lines, that is, of the direction of the axes of the optical ellipsoid lying in the symmetry plane, is so small throughout the series as to be scarcely greater than the error in the determination of the extinction angles. Hence it is ample to conduct the observations for sodium light, and in general precisely the same results were arrived at by the use of white light.

The orientations are expressed with reference to the morphological axes a and c , and also, for the sake of comparison with the work of other observers, with respect to the normals to the basal plane $c\{001\}$ and the orthopinacoid $a\{100\}$.

Optic Axial Angles.—The section plates for the determination of the optic axial angles required to be 1 or 2 mm. thick, and thicker still for most of the caesium salts, on account of the very feeble double refraction which is characteristic of the series. The measurements were made with the delicate Fuess larger axial angle apparatus. Monobromonaphthalene was usually employed as the immersion liquid in the determinations of $2Ha$ and $2Ho$. The pairs of sections, perpendicular to the first and second median lines respectively, which were employed together to furnish the data for the calculation of the true angle $2Va$ by means of the formula $\tan Va = \frac{\sin Ha}{\sin Ho}$ are numbered in the tables of results 1 and $1a$, 2 and $2a$, or 3 and $3a$.

The two series of measurements with each pair were carried out immediately in succession in the same cell of liquid, in order that no change might in the interval occur in the refractive index of the latter. The order of dispersion exhibited by the calculated results was in every case confirmed by observation of the interference figures in white light, and actual measurement in monochromatic light, when the sections perpendicular to the first median line were immersed in a liquid of about the same refractive index as the mean of the crystal indices. The approximate true angle was then being observed, and the indications were of very considerable value, as the dispersion of the optic axes for different wave-lengths of light is usually very small in this series, so much so sometimes as to approach the few minutes of error in the calculation of the true angles.

Dispersion of the Median Lines.—The stauroscope affords no trustworthy method of determining such small dispersions, of the axes of the optical ellipsoid lying in the symmetry plane, as are presented in this series. They have been determined in every case by observations in white light, and measurements in monochromatic light, while the section was immersed in a liquid of almost exactly the same refractive index as the mean index of the crystal, or successively in two liquids slightly differing from that mean, but in opposite directions. The orientation of the crystal section was first carefully noted with reference to the existing faces left on the broad edges of the section; it may be here mentioned that the grinding instrument does its work so cleanly that these faces are rarely damaged. The circle readings are then carefully noted, while each axial brush in turn is brought between the pair of cross wires for each of the five wave-lengths in succession, or at least the two extreme ones, and thus the angular dispersion of each optic axis determined. From this, of course, the position of the median line for the two extreme wave-lengths can be deduced, and, knowing the position of the faces of the crystal, the actual dispersion within the crystal ascertained. Very great care, however, is requisite in the choice of liquids in the cases of crystals exhibiting such small dispersions, rarely more than 10—15' between red light of the wave-length of the lithium line and greenish-blue light of the wave-length of the F hydrogen line, as it frequently happens that the indications in two such liquids, differing not very greatly in refractive index, exhibit considerable deviations from each other. This occurs mainly, however, in connection with the dispersion of the two axes, the dispersion of the median lines is usually the same in both.

Refractive Indices.—The refractive indices were determined by means of a new No. 1a Fuess goniometer, fitted with all the most recent improvements. The author desires to express his sincere thanks to the Government Grant Committee of the Royal Society for

their considerable grant for the purchase of this beautiful instrument, the most perfect and accurate spectrometer for use with miniature prisms procurable. The monochromatic illuminator works admirably in connection with it. A side window in the screen lined with dark velvet which is employed to shield the spectrometer from extraneous light, fitted with an easily moving shutter, and with an incandescent gas lamp placed behind it, supplied with a metal cylindrical chimney pierced by a circular aperture, 1 inch in diameter, opposite the light, serves to illuminate the circle when the shutter is opened. It is convenient to have the lamp adjustable for height on a standard rod supported by a heavy base. It can then be used as source of light during the measurement of the angle of the prism, and the subsequent approximate adjustment of the prism for minimum deviation. It is convenient to have the spectrometer mounted on a special stand whose four legs terminate in ball castors; the instrument can then be readily moved so as to bring the illumination tube of the collimator in front either of the gas lamp or the monochromatic illuminator, and it is a particularly convenient arrangement in adjusting so as to get the maximum illumination of the image of the Websky slit refracted through the prism.

Two series of observations of the angles of minimum deviation were always taken, one on each side of the incident light, that is, with the light incident on each of the prism faces in turn, and the mean considered as the true deviation. The readings rarely differed by more than two minutes.

It will be understood that the symbols under the headings "Nature of light" in the tables, mean as follows:—Li, light from the monochromatic illuminator of the same wave-length as the red lithium line; C of the wave-length of the red hydrogen line C; Na of the wave-length of the yellow D sodium lines; Tl of the thallium green line; F of the greenish-blue hydrogen line F; and G of the violet hydrogen line near G.

A general expression for any wave-length has been calculated for the intermediate index of refraction β of each salt, corrected for a vacuum; the mean of the observed values of this index for C, Na, and Tl light, corrected for a vacuum by the addition of 0.0004, have been employed in each case in calculating the formula. These formulæ reproduce the observed values (+ 0.0004) perfectly as far as F; another term would be required to yield the G values accurately, but its use would hardly compensate for its complexity. The α and γ indices are also very closely expressed by the formulæ when the first constants are diminished and increased respectively by amounts which are given for each salt. The relations of these differences from the β values determine the sign of the double refraction.

The Axial Ratios of the Optical Ellipsoid.—The relative velocities of light vibration along the three axes of the optical ellipsoid have been calculated for each salt, as in the cases of the simple sulphates previously described, by taking the ratio of the reciprocals of the three indices for any one and the same wave-length (usually sodium light). In the cases of the simple sulphates of rhombic symmetry the order of the morphological axes was taken, as these axes were coincident with the axes of the optical ellipsoid; in the present cases of the monoclinic double sulphates only one of the axes of the optical ellipsoid is coincident with a morphological axis, namely, the intermediate axis \mathfrak{b} with the symmetry axis b . The other two axes of the optical ellipsoid are only conditioned by the fact that they must lie in the symmetry plane and be at right angles to each other; their relations to the two morphological axes lying in this plane differ for each salt. It will be of just as much interest, however, to compare their ratios for the different salts; hence they have been calculated, and are arranged in the order $\mathfrak{a} : \mathfrak{b} : \mathfrak{c}$; the first being the maximum, and the third the minimum axis. Vibrations parallel to \mathfrak{a} yield the minimum refractive index α , and those parallel to \mathfrak{c} give γ . The value of \mathfrak{b} is taken as unity.

$$\text{Hence} \quad \frac{\mathfrak{a}}{\mathfrak{b}} = \frac{\beta}{\alpha} \quad \text{and} \quad \frac{\mathfrak{c}}{\mathfrak{b}} = \frac{\beta}{\gamma}.$$

It will be observed that the term optical elasticity is not employed in this communication. The important generalisation of Fletcher (*Mineral. Mag.*, 1891, 278) that the whole of the optical characters of crystals may be completely expressed with reference to the geometrical characters of a surface which is in general an ellipsoid, the optical indicatrix, renders it no longer necessary to employ terms which refer to particular versions of the undulatory theory. The term "axes of optical elasticity" employed in the communication concerning the simple sulphates is now replaced by the expression "axes of the optical ellipsoid."

The fundamental fact of Fletcher's generalisation, which is now adopted as the basis of the treatment of the optical properties of crystals by Groth (1895 edition of *Physikalische Krystallographie*), is expressed in the original memoir as follows:—

"The characters of a ray of plane-polarised homogeneous light transmitted within a medium are indicated by geometrical characters at a corresponding point on an ellipsoid; the direction of the ray is that of a diameter intersecting perpendicularly the normal drawn to the ellipsoid at the corresponding point; the velocity is inversely proportional to the length of the normal intercepted by the ray; the plane of polarisation is perpendicular to the normal."

The optical velocity ellipsoid referred to in this communication,

whose axes are the reciprocals of the refractive indices, is the polar reciprocal of the optical indicatrix, the magnitude of the axes of the two ellipsoids being inverted, the maximum axis of the velocity ellipsoid being the minimum axis of the indicatrix, and *vice versa*. As regards the axes of the velocity ellipsoid, their respective velocities refer to the vibrations, not to the transmission, of light along those directions.

Molecular Optical Constants.—These constants, afforded by the formulæ of Lorenz and of Gladstone and Dale, have been calculated for each salt from the data afforded by the determinations of density and of refractive index. It must be remembered that the same remark applies to these constants as to the axial ratios of the optical ellipsoid; the directions within the crystals are only identical throughout the series in the case of the values for *b*, which is coincident with the symmetry axis; the directions of *a* and *c* differ somewhat in the various members of the series.

Observations of Optic Axial Angle and of Refraction at Higher Temperatures.—The salts of this series, containing as they do water of crystallisation, cannot naturally be heated to 100° or more without decomposition. Most of them, however, have been found to withstand a temperature of 70° sufficiently long before becoming opaque to enable measurements of the apparent optic axial angle in air and of refractive index to be carried out. The apparatus employed for the observation of the interference figures at 70° was the ordinary air bath arrangement, furnished with two thermometers, supplied by Fuess with the larger optic axial angle goniometer. For the determinations of refractive index at higher temperatures, the latest form of heating apparatus supplied with the No. 1a goniometer was employed; this admirable arrangement is described by Fuess in the *Neues Jahrbuch für Mineralogie*, 1890, **1**, 161. The whole of the salts could not be investigated as regards their refraction at higher temperatures by means of uncovered prisms, on account of deterioration of the ground surfaces. In most cases this difficulty was overcome by using prisms fitted with cemented cover-glasses, and when equilibrium had been established at the particular higher temperature, taking a series of alternate observations for sodium light of minimum deviation and the prism angle; it was generally found possible to obtain at least two pairs of constant readings before opacity supervened.

Analyses of all the salts employed in this investigation, of a satisfactory character, were given in the former communication concerning the morphology of the series, so that there can be no question as to their purity or identity.

SALTS CONTAINING MAGNESIUM.

Potassium Magnesium Sulphate, $K_2Mg(SO_4)_2 \cdot 6H_2O$.

The crystals of this salt *cleave* readily parallel to the orthodome $r'\{201\}$, as stated by Topsøe and Christiansen. The cleaved surfaces yield sharp single images of the goniometer slit, and the circle reading corresponding was exactly 180° from that of the image afforded by the remaining r' face, in each of the cases investigated.

Volume.

Relative Density.—Four determinations were made with four separate crops of clear, well-formed crystals, two being taken from each of two distinct preparations. Every individual crystal used to make up the quantity taken for each determination was verified by careful inspection of its faces with a lens, in order to avoid the possibility of any admixture with the sparingly soluble sulphate of potassium, which is apt to crystallise out if it is in the slightest excess. One preparation was that used for the goniometrical work described in the previous communication, and the other was an independent one similarly prepared by quantitative admixture of the pure component sulphates. The following results were obtained.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3.3397	2.0274
2.8918	2.0272
4.2998	2.0279
1.8775	2.0282
Mean....	<u>2.0277</u>

Joule and Playfair obtained 2.053. Perrot obtained numbers varying from 2.018 to 2.075, affording as mean 2.04.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{402}{2.028} = 198.23.$$

Distance Ratios (Topic Axes).—It was shown in the former communication concerning the morphology that the axial angle $\beta = 75^\circ 12'$ and

$$a : b : c = 0.7413 : 1 : 0.4993.$$

Combining these with the molecular volume, as described in the introduction, we obtain for the distance ratios—

$$\chi : \psi : \omega = 6.0881 : 8.2128 : 4.1006.$$

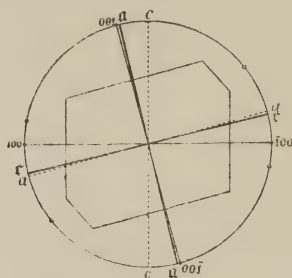
Optics.

The optical properties of potassium magnesium sulphate were partially studied by Murmann and Rotter (*loc. cit.*). The plane of

the optic axes is the symmetry plane $b\{010\}$, as is general throughout the series.

Orientation of Axes of Optical Ellipsoid.—The directions of extinction in the symmetry plane were determined on two polished section-plates ground parallel to $b\{010\}$. Extinction occurred in the two cases at $1^\circ 5'$ and $1^\circ 15'$ respectively from the direction of the normal to $c\{001\}$, and on that side of the latter nearest the vertical axis c of the crystal as indicated in the accompanying figure (Fig. 1). The mean value, $1^\circ 10'$, is taken to represent the direction of extinction. Murmann and Rotter give $1^\circ 0'$.

FIG. 1.



Examination of section-plates ground perpendicular respectively to this direction, and to the direction at right angles to it in the symmetry plane, show that this is the direction of the second median line, the direction at right angles to it in the symmetry plane being the first median line.

The *double refraction*, determined by means of a quarter undulation mica plate when examining in convergent polarised light the section-plate perpendicular to the first median line, and confirmed later by the relation of the three indices of refraction, is of positive sign, as stated by other observers. Hence the first median line is the minimum axis of the optical ellipsoid ϵ , and the second median line the maximum a . The intermediate axis b is coincident with the symmetry axis b .

It was shown in the previous communication that the morphological axial angle ac is $75^\circ 12'$. Hence—

The first median line ϵ makes an angle of $1^\circ 10'$ with the crystallographical axis a , and the second median line a makes an angle of $13^\circ 38'$ with the vertical axis c , both median lines lying in the obtuse angle of the axes a and c .

The first median line is also inclined $88^\circ 50'$ to the normal to $c\{001\}$, and $13^\circ 38'$ to the normal to $a\{100\}$. Murmann and Rotter, using their value of ac , gave $1^\circ 0'$, $13^\circ 55'$, and $89^\circ 0'$ for the corre-

sponding angles. Topsøe and Christiansen gave $0^{\circ} 30'$, $14^{\circ} 25'$, and $89^{\circ} 30'$.

In Fig. 1, and all the subsequent figures representing the orientations, the positions of the optic axes are indicated by small rings.

Optic Axial Angle.—Three pairs of section-plates were ground and polished accurately perpendicular to the first and second median lines. The plates obtained of the thickness stated in the introduction gave excellent definition. The dispersion is very small, almost nil for the apparent angle in air as seen in white light, one of the brushes being colourless and the other very nearly so, being faintly bordered with red outside and blue inside. The small amount of dispersion was clearly visible, however, when the monochromatic light apparatus was employed and the prism rotated so as to obtain light first from one end of the spectrum and then from the other. The accompanying tables give the results of the measurements of 2E, the apparent angle in air, of 2Ha, the apparent acute, and 2Ho, the apparent obtuse angle in monobromonaphthalene, and of the calculations of the true angle 2Va therefrom.

Determination of apparent Angle in Air of Potassium Magnesium Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li.....	$72^{\circ} 51'$	$72^{\circ} 35'$	$72^{\circ} 43'$	$72^{\circ} 43'$
C.....	$72 52$	$72 36$	$72 44$	$72 44$
Na.....	$72 54$	$72 40$	$72 47$	$72 47$
Tl.....	$72 56$	$72 43$	$72 51$	$72 50$
F.....	$72 59$	$72 47$	$72 56$	$72 54$

Determination of true Optic Axial Angle of Potassium Magnesium Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated value of 2Va.	Mean value of 2Va.
Li.....	{ 1	$42^{\circ} 16'$	1a	$107^{\circ} 52'$	$48^{\circ} 5'$	$48^{\circ} 0'$
	{ 2	$42 13$	2a	$107 53$	$48 2$	
	{ 3	$42 10$	3a	$108 10$	$47 54$	
C.....	{ 1	$42 15$	1a	$107 50$	$48 4$	$47 59$
	{ 2	$42 9$	2a	$107 40$	$48 1$	
	{ 3	$42 5$	3a	$108 2$	$47 52$	
Na.....	{ 1	$42 2$	1a	$107 20$	$48 0$	$47 54$
	{ 2	$41 54$	2a	$107 4$	$47 56$	
	{ 3	$41 51$	3a	$107 34$	$47 46$	
Tl.....	{ 1	$41 46$	1a	$106 42$	$47 55$	$47 48$
	{ 2	$41 38$	2a	$106 30$	$47 50$	
	{ 3	$41 35$	3a	$107 0$	$47 39$	
F.....	{ 1	$41 29$	1a	$106 0$	$47 50$	$47 40$
	{ 2	$41 19$	2a	$105 50$	$47 43$	
	{ 3	$41 15$	3a	$106 39$	$47 26$	

The true angle was not determined directly by Murmann and Rotter, but was calculated from the acute angle in oil and the medium refractive index β ; the value thus obtained was $48^\circ 21'$, presumably for sodium light. As pointed out in the communication concerning the simple normal sulphates (*loc. cit.*, 671), such calculated values cannot have the value of direct observations with a complementary pair of sections. Murmann and Rotter state that the apparent angle in air is smaller for red than for blue, although no measurements for different colours were carried out, and that the true angle, judged from the observation in oil, is larger for red than for blue; this agrees completely with the above results. Topsøe and Christiansen give $47^\circ 59'$ as the angle for sodium light.

The order of dispersion of the optic axes was confirmed by an observation in turpentine, whose index of refraction is only very slightly greater than the mean index of the crystals of this salt. The angle observed for C light was $47^\circ 41'$, for sodium light $47^\circ 33'$, and for thallium light $47^\circ 26'$.

Dispersion of the Median Lines.—The observation of the interference figure exhibited in turpentine by a section perpendicular to the first median line affords a means of ascertaining the dispersion of the median lines. This dispersion is so slight that the stauroscope affords no certain evidence of it. The figure in turpentine exhibits the inclined dispersion very clearly. One of the hyperbolic brushes is almost free from colour when white light is employed, while the other is fringed with blue outside and red within, indicating the greater inclination of the axes for red, and that one of the axes remains practically stationary for all colours. A careful series of determinations with the aid of the purest monochromatic light showed a dispersion of this axis of only $3'$, whilst the other was dispersed $18'$, between C and Tl light. The median lines must therefore be dispersed between Li and F, in accordance with the mean values derived above for the true angle ($48^\circ 0'$ to $47^\circ 40'$), about $10'$. On observing carefully the orientation of the section, which retained the natural faces on its edges unimpaired by the grinding, it was found that the axis which showed coincidence for all colours was the one which passed between the normals to $a\{100\}$ and $r\{201\}$ (nearer to the former), while the axis which showed dispersion was the one emerging approximately normal to $r'\{201\}$.

Hence the first median line lies nearer to the crystallographic axis a by about $10'$ for red than it does for blue. This agrees with the observation of Murmann and Rotter, who record no measurement, however, of the amount of the dispersion.

Effect of Rise of Temperature on the Optic Axial Angle.—The apparent angle in air was measured at 80° on Section 2. It was found to

be $75^{\circ} 10'$ for sodium light, the dispersion remaining about the same. Hence the apparent optic axial angle in air increases about $2\frac{1}{2}^{\circ}$ for 60° rise of temperature. The section remained unimpaired at this temperature during the time occupied by the observation.

Refractive Indices.—The indices of refraction were determined by means of six prisms, two being ground upon each of three clear and well-formed crystals, the directions being such that each prism yielded two indices, as described in the foregoing description of the method of work. The results are as follows.

Determinations of Refractive Indices of Potassium Magnesium Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Mean refractive index.	Values of Topsøe and Christiansen.
α Vibrations parallel 2nd median line	Li	1.4581	1.4581	1.4580	1.4581	—
	C	1.4585	1.4586	1.4585	1.4585	1.4582
	Na	1.4605	1.4607	1.4608	1.4607	1.4602
	Tl	1.4630	1.4631	1.4631	1.4631	—
	F	1.4655	1.4659	1.4659	1.4658	1.4649
	G	1.4698	—	1.4700	1.4699	—
β Vibrations parallel symmetry axis b	Li	1.4602	1.4603	1.4604	1.4603	—
	C	1.4606	1.4609	1.4607	1.4607	1.4610
	Na	1.4628	1.4628	1.4631	1.4629	1.4633
	Tl	1.4652	1.4651	1.4653	1.4652	—
	F	1.4677	1.4679	1.4679	1.4678	1.4682
	G	1.4720	—	1.4720	1.4720	—
γ Vibrations parallel 1st median line	Li	1.4729	1.4725	1.4728	1.4727	—
	C	1.4733	1.4729	1.4731	1.4731	1.4743
	Na	1.4759	1.4752	1.4754	1.4755	1.4768
	Tl	1.4780	1.4775	1.4778	1.4778	—
	F	1.4810	1.4808	1.4811	1.4810	1.4827
	G	1.4853	—	1.4852	1.4853	—

The intermediate index of refraction β (in a vacuum) is accurately expressed for any wave-length λ as far as F in the spectrum by the formula

$$\beta = 1.4508 + \frac{483 \ 699}{\lambda^2} - \frac{1 \ 727 \ 800 \ 000 \ 000}{\lambda^4} + \dots$$

The α indices are very closely reproduced if the constant 1.4508 is diminished by 0.0022, and the γ indices if the constant is increased by 0.0126, the closer approximation of the β values to those of determining the positive nature of the double refraction.

The only indices of refraction given by Murmann and Rotter are four values of β , namely, for red (no specific wave-length) 1.468, for

yellow 1·470, for green 1·474, and for blue 1·476. These numbers are much too high, they are even higher than those of the rubidium salt, as determined both by the author and by Perrot, and it will be shown that throughout the series the indices of the rubidium salt are always higher than those of the potassium salt. The values given by Topsøe and Christiansen are shown in the last column in the table; only the β indices were determined directly, and the indirectly determined values of α and γ are seen to be considerably out of agreement with the directly determined indices now given.

Alteration of Refraction by Increase of Temperature.—A number of determinations were made with three of the prisms at 70°. Owing to the rapidity with which efflorescence occurs when the crystals of this series are warmed the refracted images of the slit rapidly deteriorate, so that the same reliance cannot be placed on the observations as at the ordinary temperature. Hence the complete series of numbers obtained for the various wave-lengths could not fairly be taken as evidence of minute changes of dispersion. But the whole series agree in indicating that each index of refraction is lowered about 0·0019 (the limits being 0·0015—0·0022) by a rise of 50° (from 18° to 70°) of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—These ratios calculated from the reciprocals of the refractive indices for sodium light are as follows.

$$a : b : c = 1.0015 : 1 : 0.9915.$$

The ratios calculated from the values for other wave-lengths are practically identical with these.

Molecular Optical Constants.—The following are the refraction constants, calculated by means of the Lorenz formula, for the rays C and G.

Axis of optical ellipsoid	α .	β .	γ .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$	{ C. 0.1348	0.1353	0.1385
	{ G. 0.1377	0.1382	0.1415
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C. 54.18	54.40	55.66
	{ G. 55.34	55.55	56.88

The dispersion constants are as under—

Specific dispersion, $n_G - n_C$	0.0029	0.0029	0.0030
Molecular dispersion, $m_G - m_C$	1.16	1.15	1.22

The following are the values of the molecular refraction calculated from the formula of Gladstone and Dale for the wave-length of the red hydrogen line C.

$$\text{Molecular refraction, } \frac{n - 1}{d} M \dots\dots\dots 90.97 \quad 91.40 \quad 93.86$$

As the refraction diminishes with rise of temperature, that is similarly to the density, all these values will remain sensibly constant for all temperatures at which the salt is capable of existing.

Rubidium Magnesium Sulphate, $\text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

There is an excellent *cleavage* parallel, $r'\{201\}$. In the cases examined the cleaved surfaces yielded single sharp images of the goniometer signal, at exactly 180° from the remaining r' face.

Volume.

Relative Density.—The following are the results of four determinations made with separate crops of well-formed crystals belonging to two different preparations. One of these preparations was that made for the goniometrical work previously published; the other was a later preparation, the rubidium sulphate employed for which was supplied by Merck, as stated in the introduction, and ascertained to be of equal purity to the earlier stock. It was, moreover, several times recrystallised.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3.5051	2.3773
3.4360	2.3841
4.2037	2.3818
4.3690	2.3856

Mean 2.3822

Perrot obtained a mean of 2.41 at 15° , the individual determinations varying from 2.377 to 2.438.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{494.4}{2.382} = 207.56.$$

Distance Ratios.—It was previously shown that the axial angle β was $74^\circ 1'$, and that

$$a : b : c = 0.7400 : 1 : 0.4975.$$

Combining these with the molecular volume, the distance ratios obtained are

$$\chi : \psi : w = 6.1941 : 8.3705 : 4.1643.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—The directions of extinction in the symmetry plane were determined staurosopically with three section-plates ground accurately parallel to the symmetry plane $b\{010\}$. The first two gave results differing so much from the direction found by Perrot that a third was ground upon an excellent crystal derived from the later preparation containing rubidium

Determination of apparent Angle in Air of Rubidium Magnesium Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li.....	75° 5'	75° 15'	75° 25'	75° 15'
C.....	75 0	75 10	75 20	75 10
Na	74 35	74 35	74 50	74 40
Tl.....	74 10	74 0	74 20	74 10
F.....	73 30	73 0	73 30	73 20

Perrot gives 76° 40' for the apparent angle in red light.

The following are the measurements of the apparent acute angle in monobromonaphthalene, carried out with the same three sections, and of the apparent obtuse angle in the same liquid, carried out with three section-plates ground perpendicular to the second median line, together with the values of the true internal angle calculated therefrom.

Determination of true Optic Axial Angle of Rubidium Magnesium Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2H α .	No. of section perp. 2nd median line.	Observed values of 2H α .	Calculated values of 2V α .	Mean value of 2V α .
Li.....	1	43° 20'	1a	108° 5'	49° 2'	49° 6'
	2	43 20	2a	107 35	49 10	
	3	43 15	3a	107 35	49 5	
C.....	1	43 15	1a	108 0	48 58	49 2
	2	43 15	2a	107 30	49 6	
	3	43 10	3a	107 30	49 2	
Na.....	1	42 50	1a	107 30	48 44	48 46
	2	42 45	2a	107 10	48 43	
	3	42 50	3a	107 5	48 50	
Tl.....	1	42 24	1a	106 50	48 30	48 29
	2	42 25	2a	106 40	48 32	
	3	42 15	3a	106 35	48 24	
F.....	1	41 50	1a	106 0	48 10	48 10
	2	41 50	2a	106 0	48 10	
	3	41 50	3a	106 0	48 10	

Sections 1 and 1a were ground upon the same crystal, this being possible because of the very feeble double refraction, which necessitates thick sections in order to afford interference figures with small rings and well-defined brushes.

Perrot obtained 50° 2' for orange-red with one section, and 49° 30' for yellow light with another, with the aid of the knowledge of the mean refractive index of the substance.

Dispersion of the Median Lines.—The dispersion of the median lines is again too small to be measured with certainty by the stauroscope. It was determined by observation of the interference figures afforded by the sections perpendicular to the first median line in turpentine,

whose refractive index is very near the mean of the indices of the crystal. The fact that the optic axial angle for red is greater than that for blue was confirmed; one of the brushes was practically devoid of colour when observed in white light, whilst the other was coloured red on the inner side nearest the stationary axis, and blue outside. On measuring the angles for C and Tl light, the readings for the axis whose brush is colourless in white light were found to be identical, whilst those for the other axis differed by $16'$. The constant axis was, as in the case of the potassium salt, the one nearly normal to $a\{100\}$, the movable axis being approximately normal to $r'\{201\}$, and further removed from the median line for red than for blue.

Hence the first median line lies nearer to the crystallographic axis a for blue than it does for red, and the amount of dispersion between Li and F would appear from the table to be about $20'$.

Effect of Rise of Temperature on the Optic Axial Angle.—Several measurements of the apparent optical axial angle in air were made at 80° for sodium light, and all the values obtained were within a third of a degree of $74^\circ 40'$, the angle at the ordinary temperature. Hence any change of angle for 60° rise of temperature falls within the limits of error of observation.

Refractive Indices.—Six prisms were employed, three being ground on one and the same crystal, yielding one value of α , two of β , and

Determination of Refractive Indices of Rubidium Magnesium Sulphate.

Index.	Nature of light.	Crystal 1, 3 prisms.	Crystal 2, 1 prism.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.	Perrot's values.
α Vibs. par. 2nd median line α	Li	1.4648	—	1.4646	1.4645	1.4646	—
	C	1.4651	—	1.4650	1.4649	1.4650	1.4648
	Na	1.4672	—	1.4672	1.4671	1.4672	1.4670
	Tl	1.4696	—	1.4695	1.4695	1.4695	—
	F	1.4723	—	1.4724	1.4725	1.4724	1.4721
	G	1.4760	—	—	1.4764	1.4762	—
β Vibs. par. symmetry axis $b(b)$	Li	1.4659	1.4666	1.4665	1.4664	1.4664	—
	C	1.4664	1.4670	1.4669	1.4668	1.4668	1.4667
	Na	1.4686	1.4689	1.4691	1.4688	1.4689	1.4690
	Tl	1.4708	1.4716	1.4714	1.4712	1.4713	—
	F	1.4739	1.4747	1.4743	1.4743	1.4743	1.4739
	G	1.4780	1.4785	—	1.4781	1.4782	—
γ Vibs. par. 1st median line γ	Li	1.4753	1.4758	—	—	1.4755	—
	C	1.4757	1.4762	—	—	1.4759	1.4756
	Na	1.4779	1.4780	—	—	1.4779	1.4782
	Tl	1.4802	1.4808	—	—	1.4805	—
	F	1.4833	1.4837	—	—	1.4835	1.4833
	G	1.4874	1.4878	—	—	1.4876	—

three of γ , and the other three being ground upon three other separate crystals. The results are as follows.

The intermediate index β , reduced to a vacuum, is exactly expressed, for any wave-length λ as far as F, by the formula

$$\beta = 1.4592 + \frac{318\ 735}{\lambda^2} + \frac{1\ 105\ 200\ 000\ 000}{\lambda^4} + \dots$$

The α indices are also very closely reproduced by the formula if the constant 1.4592 is diminished by 0.0018, and the γ indices if it is increased by 0.0091, the β indices being thus nearest to the α values, in accordance with the positive sign of double refraction.

It will be observed that the indices given by Perrot agree very closely with the numbers now given.

Alteration of Refraction by Increase of Temperature.—Measurements with two prisms at 70° indicated that the indices are lowered by about 0.0015 for an increase of 50° of temperature, the dispersion remaining sensibly the same.

Ratio of Axes of Optical Velocity Ellipsoid.—The calculated values of these ratios are

$$a : b : c = 1.0012 : 1 : 0.9939.$$

Molecular Optical Constants.—These are as follows.

Axis of optical ellipsoid.....	α .	β .	γ .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$	C. 0.1161	0.1165	0.1185
	G. 0.1185	0.1190	0.1210
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	C. 57.42	57.61	58.57
	G. 58.60	58.82	59.80
Specific dispersion, $n_G - n_C$	0.0024	0.0025	0.0025
Molecular dispersion, $m_G - m_C$	1.18	1.21	1.23
Molecular refraction, $\frac{n - 1}{d} M$	C 96.60	96.97	98.86

These values will hold good for all temperatures at which the salt is capable of existing, as the refraction and density are similarly affected by change of temperature.

Cæsium Magnesium Sulphate, $\text{Cs}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Among the large number of crops of cæsium magnesium sulphate obtained for the purposes of the volume and optical work, several were observed to consist of crystals exhibiting well-developed faces of the orthodome $r(201) - 2P_\infty$, a form not included in the list given for this salt in the previous communication concerning the morphology of the series (*loc. cit.*, 350). There is a good cleavage parallel $r'\{201\}$, the fractures yielding well-defined

single images of the goniometer signal at exactly 180° to the r' face remaining on the part of the crystal examined.

Volume.

Relative Density.—The following are the results of four determinations made with different crops of excellent clear crystals of this salt.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.4357	2.6694
4.1772	2.6728
4.5400	2.6688
3.0734	2.6706

Mean 2.6704

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{589.4}{2.67} = 220.75.$$

Distance Ratios.—The axial angle β was previously shown to be $72^\circ 54'$, and

$$a : b : c = 0.7279 : 1 : 0.4946.$$

Combining these with the molecular volume, we obtain

$$\chi : \psi : w = 6.2778 : 8.6246 : 4.2657.$$

Optics.

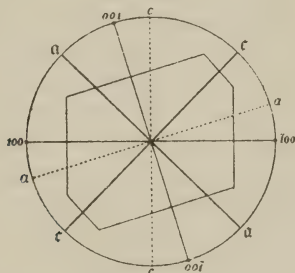
Cæsium magnesium sulphate exhibits most interesting and exceptional optical properties, including the phenomenon of crossed axial plane dispersion, accompanied by great sensitiveness of the optic axial angle to change of wave-length in the illuminating light and to temperature, together with remarkable refraction phenomena. It is very similar indeed to the case of normal rubidium sulphate described in the communication on the normal sulphates (*loc. cit.*, 680), and the reason for these exceptional properties will be subsequently shown to be equally interesting and important when the three salts containing magnesium are compared.

Orientation of Axes of Optical Ellipsoid.—The directions of extinction in the symmetry plane were determined on two sections ground parallel to the symmetry plane $b\{010\}$. Extinction occurs much further removed, forwards and downwards in the upper front octant, from the normal to the basal plane than in the rubidium and potassium salts, as represented in Fig. 3. The two sections indicated respectively extinction angles of $29^\circ 40'$ and $29^\circ 35'$ with the normal to $c\{001\}$. The mean value $29^\circ 37'$ may be taken as representing the true extinction angle.

On proceeding to grind section-plates perpendicular to the directions of the two axes of the optical ellipsoid indicated by the extinc-

tion determination, it was found that the one nearest the normal to $c\{001\}$ is, as in the other magnesium salts, the second median line, the other at right angles to this, also lying in the symmetry plane, is the first median line. This statement, however, as regards the second

FIG. 3.



median line will be shown to hold only for light ranging from the red end of the spectrum to a wave-length in the blue between F and G; for rays beyond this, the symmetry axis b , the intermediate axis b of the optical ellipsoid is the second median line. With this reservation, the orientation of the axes may be stated in a similar manner to that of the potassium and rubidium salts.

The *double refraction* is of positive sign, determined by the quarter undulation mica plate, and subsequently confirmed by the relations of the refractive indices. The axial angle, ac , was previously given (*loc. cit.*) as $72^\circ 54'$. The orientations are therefore as follows.

The first median line c lies in the acute angle of the morphological axes a and c , and makes an angle of $29^\circ 37'$ with the axis a .

The second median line a lies in the obtuse angle ac , and makes an angle of $46^\circ 43'$ with the vertical axis c .

The first median line is also inclined $119^\circ 37'$ to the normal to $c\{001\}$, and $46^\circ 43'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Section-plates perpendicular to the first median line require to be very thick in order to afford well-defined interference figures, owing to the extremely small double refraction. Three were ground of respectively 2, $4\frac{1}{2}$, and 5 mm. thickness, the latter being about a suitable thickness. It may be useful to briefly mention, as an example of how the section-plates were prepared during the whole of this work, the manner in which the crystals of cæsium magnesium sulphate were adjusted upon the grinding instrument for the purpose of preparing the sections perpendicular to the first median line. The crystal was cemented upon the rotatable crystal holder, so that the well-defined zone of faces bqc (see previous memoir for figure, p. 350) was approximately vertical, and the face c about

parallel to the lower tangent screw of the graduated adjusting apparatus. The zone of faces was then adjusted by use of the goniometrical telescope and collimator, exactly perpendicular to the grinding plane, and the face $c\{001\}$ exactly parallel to the lower tangent screw by adjustment of the rotatable cylinder of the crystal holder. Both these adjustments being perfected, the upper tangent screw, which was parallel to the normal to $c\{001\}$, was rotated for the extinction angle $29^{\circ} 37'$ in the direction required by the foregoing data to bring the first median line perpendicular to the grinding table. The first surface of the section-plate was then ground, and the second surface subsequently, either by use of the arrangement for grinding a parallel surface or in a like manner to the first.

The interference figure afforded by such a section of caesium magnesium sulphate in convergent polarised white light is quite different to that of the corresponding potassium and rubidium salts, and very similar to that of normal rubidium sulphate. It exhibits evidence of large dispersion of the optic axes; the hyperbolic brushes are broad spectrum bands with dark centres. When the monochromatic illuminator is used, it is observed that the brushes are separated about 25° for the extreme red, and approach each other more and more as the wave-length is diminished, until for a colour in the blue between F and G they unite in the centre, and the uniaxial cross and rings are produced; further reduction of the wave-length then causes the brushes to separate in the direction at right angles to their former one, the second median line changing from the other axis of the ellipsoid lying in the symmetry plane to the morphological symmetry axis normal to the symmetry plane.

In the photographic reproduction of the interference figures of normal rubidium sulphate, given opposite p. 691 of the communication concerning the three normal sulphates (*loc. cit.*), Nos. 1, 2, 3, 4, 5, 6, and 7 represent almost exactly what was observed. No. 1 resembles the figure for Li light when the small-angle polariscopical goniometer used for exact measurements is employed, No. 2 that for C light, No. 3 for Na, No. 4 for Tl, No. 5 for F, No. 6 for the wave-length in the blue for which the uniaxial cross is produced, and No. 7 the figure for G light, with the axes separated in the vertical plane.

The following measurements of the apparent angle in air were obtained (p. 369).

The measurements for G were carried out with the plate rotated 90° in its own plane from the position occupied while making the measurements as far as F. The determination of the wave-length for which the uniaxial cross was produced was made by taking the reading of the prism circle of the monochromatic light apparatus for the

Determination of apparent Angle in Air of Cæsium Magnesium Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.	
Li.....	25° 40'	25° 30'	25° 50'	25° 40'	} In sym- metry plane.
C.....	25 5	25 10	25 30	25 15	
Na.....	22 55	22 45	22 50	22 50	
Tl.....	19 0	19 20	19 10	19 10	
F.....	13 30	13 15	13 15	13 20	
Wave-length 450.	Coincident.	Coincident.	Coincident.	Coincident.	
G.....	12 0	13 0	14 30	13 10	} In plane at right angles.

coincident position of the optic axes, and ascertaining the corresponding wave-length from the curve referred to in the memoir describing the monochromatic light apparatus. The readiness with which this determination may be made is one of the great advantages of that apparatus. The prism circle reading was taken in each case first while the plate was arranged for the measurements in the symmetry plane, and again when arranged in the position at right angles, after the measurements for G light had been carried out. The mean of each pair was then taken, and as the three means were all very close together, the limiting wave-lengths being 446 to 454, the mean 450 is given as the wave-length for coincidence.

The optic axial angle is too small to enable the obtuse angle to be seen through a plate perpendicular to the second median line, even in monobromonaphthalene. Hence the same plan has been adopted as was used in the case of rubidium sulphate of determining the true angle by observations of the apparent angle when immersed in two liquids whose refractive indices are very nearly, and the mean exactly equal to the mean refractive index of the crystal. Such liquids are turpentine ($\mu_D = 1.48$) and toluene ($\mu_D = 1.491$).

The interference figures as seen in white light while immersed in these liquids are very beautiful. When the monochromatic illuminator is employed, the brushes are sharp and clearly separated for red light, with a section 5 mm. thick, and surrounded by several rings; as the light is changed through orange and yellow to green, they approach each other, and eventually coalesce for a shade of blue, forming a sharp uniaxial cross surrounded by several circles, and as violet is approached they again separate in the plane at right angles, as in case of the apparent angle in air.

The measured angles are given in the following table. Sections 2 and 3 were employed, Section 1 not being so thick, and the figures, therefore, not so clearly defined.

Determination of the true Optic Axial Angle of Cæsium Magnesium Sulphate by Immersion in Turpentine and Toluene.

Nature of light.	No. of section.	In turpentine.	In toluene.	Mean.	Mean value of $2V_a$.	In symmetry plane.
Li.....	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 18^\circ 20' \\ 18 \ 20 \end{matrix}$	$\begin{matrix} 18^\circ 10' \\ 17 \ 50 \end{matrix}$	$\begin{matrix} 18^\circ 15' \\ 18 \ 5 \end{matrix}$	$\begin{matrix} 18^\circ 10' \\ 18 \ 0 \end{matrix}$	
C	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 18 \ 5 \\ 18 \ 10 \end{matrix}$	$\begin{matrix} 18 \ 5 \\ 17 \ 40 \end{matrix}$	$\begin{matrix} 18 \ 5 \\ 17 \ 55 \end{matrix}$	$\begin{matrix} 18 \ 0 \\ 16 \ 25 \end{matrix}$	
Na	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 16 \ 50 \\ 16 \ 20 \end{matrix}$	$\begin{matrix} 16 \ 30 \\ 16 \ 10 \end{matrix}$	$\begin{matrix} 16 \ 40 \\ 16 \ 15 \end{matrix}$	$\begin{matrix} 16 \ 25 \\ 14 \ 20 \end{matrix}$	
Tl.....	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 14 \ 50 \\ 14 \ 20 \end{matrix}$	$\begin{matrix} 14 \ 30 \\ 13 \ 50 \end{matrix}$	$\begin{matrix} 14 \ 40 \\ 14 \ 5 \end{matrix}$	$\begin{matrix} 14 \ 20 \\ 11 \ 15 \end{matrix}$	
F	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 12 \ 10 \\ 10 \ 40 \end{matrix}$	$\begin{matrix} 12 \ 0 \\ 10 \ 20 \end{matrix}$	$\begin{matrix} 12 \ 5 \\ 10 \ 30 \end{matrix}$	$\begin{matrix} 11 \ 15 \end{matrix}$	
Wave-length in blue.	2 and 3. Coincident. Coincident.					
G.....	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{matrix} 6^\circ 20' \\ 7 \ 20 \end{matrix}$	$\begin{matrix} 6^\circ 40' \\ 7 \ 40 \end{matrix}$	$\begin{matrix} 6^\circ 30' \\ 7 \ 30 \end{matrix}$	$\begin{matrix} 7^\circ 0' \end{matrix}$	In plane at right angles.

The readings of the prism circle for the wave-length in the blue for which the axes coincided with the first median line were as follows.

	In turpentine.	In toluene.	Mean.	Mean prism circle reading for coincidence.
Section 2	6° 35'	6° 45'	6° 40'	6° 22'
Section 3	6 10	6 0	6 5	

The reading 6° 22' of the prism circle corresponds to the passage of light of the wave-length 450 through the exit slit of the monochromatic light apparatus, the same as was found for the production of the uniaxial figure in air, and for this wave-length the crystals of cæsium magnesium sulphate simulate the optical properties of uniaxial crystals.

Dispersion of the Median Lines.—As is the case with the optic axial angle, the order of dispersion of the median lines is exceptional for this salt. The differences between the readings for each axis indicate that the first median line is nearer to the crystallographic axis *a* for lithium light by about 20' than it is for F light. The dispersion of each axis is large, and is largest for the one lying nearest to the crystallographic axis *a*.

Effect of Rise of Temperature on the Optic Axial Angle.—The optical behaviour of the crystals of this salt when their temperature is raised is particularly interesting. Both plates 2 and 3 were heated, and the phenomena carefully followed. As soon as the temperature begins to rise, the axes commence to approach each other. At 50°, with both

plates, the axes coalesced and the uniaxial cross was produced for F light. At 70° , the cross was produced for Tl light, the axes being dispersed for F light in the vertical plane at right angles, while for Na light they were still separated in the horizontal plane by $12^\circ 40'$, for C light by $17^\circ 5'$, and for Li light by $18^\circ 0'$. At 85° , the axes were united to form the cross for Na light. The valuable section 3 of 5 mm. thickness was not heated higher, but section 2 was further studied. At 100° , the axes were crossed for C light, and finally at 103° the uniaxial cross was produced for Li light, the dispersion of the axes occurring now entirely in the vertical plane. For the short time at which the temperature was maintained so high the crystal was not perceptibly injured. On cooling, the phenomena recurred in the reverse order, but it was found, on again measuring the angles at the ordinary temperature some days afterwards, that the separation of the axes had been permanently diminished by about $40'$, and on heating again the cross was produced for the various colours at slightly lower temperatures than on the occasion of the first heating.

Refractive Indices.—The exceptional optic axial angle phenomena of cæsium magnesium sulphate, resembling the phenomena presented by rubidium sulphate, although a more extreme case, is due to a similar cause to that obtaining in the case of the latter salt; namely, double refraction so feeble that one of the extreme axes of the optical ellipsoid falls nearly coincident with the intermediate axis *b*. The double refraction being positive, and the first median line consequently being *c*, the minimum axis of the optical ellipsoid, it is the maximum axis *a* which is nearly coincident with *b*. The similarity of the cases of Rb_2SO_4 and the salt now under discussion indicated the probability of this, and that it is the fact was at once revealed on examination of a prism ground so as to furnish the two refractive indices α and β , corresponding to the two axes *a* and *b*. Such a prism, as in the case of Rb_2SO_4 , exhibited only one refracted image of the slit instead of two as usual. This image, however, had the peculiarity shown by the analogous one of rubidium sulphate that it remained visible in all positions of the nicol prism carried in front of the eyepiece of the spectrometer. It was, in fact, a case of two overlapping images, one extinguishing at 0° and the other at 90° . On replacing the ordinary eyepiece by the higher power eyepiece and illuminating with C light, two images were distinctly seen, differing in position by one minute of arc, corresponding to a difference of 0.0002 in refractive index. This difference diminished with the wave-length of the illuminating light, and for F light the two images were absolutely coincident as far as observation could be carried. This is in accordance with the optic axial angle phenomena, for beyond F, for wave-length 450, *a* and *b* are coincident and the

crystal is apparently uniaxial. Beyond this the directions of **a** and **b** are reversed, the symmetry axis **b** is no longer **b** but **a**, and gives the least refractive index α . Unfortunately, G light is relatively so weak in luminosity that an observer cannot be quite sure of a difference of 1' in position of the G images, but there can be no doubt whatever that the two images will be again separated, and that the one which was formerly right will now be left, and *vice versa*.

Three such prisms were ground, and the phenomena were identical with each. They were ground so that the refracting edge in each case was parallel to the symmetry axis **b**, and the faces equally inclined to the plane containing this axis **b** (optical ellipsoidal axis **b**) and the axis **a** of the optical ellipsoid. Hence the image which extinguished at 0° of the nicol was that affording α , and that extinguishing at 90° gave β . Three other prisms were likewise ground affording β and γ .

In order that there should be no doubt whatever about the relative values of α and β , calculations have been made of the value of α , assuming the accuracy of β which was afforded six times by the prisms and the mean value of which is therefore indubitable, from the measured values of β , γ , and the optic axial angle $2Va$ by means of the formula

$$\cos Va = \sqrt{\frac{1 - \frac{1}{\beta^2}}{1 - \frac{1}{\gamma^2}}}.$$

Such a calculation, as shown in the case of rubidium sulphate, affords accurate information.

The results of the calculations, assuming $\beta_{Li} = 1.4830$ and $\beta_F = 1.4912$, are

$$\alpha_{Li} = 1.48286 \quad \text{and} \quad \alpha_F = 1.49122.$$

Hence α and β differ by between 0.0001 and 0.0002 for lithium light, and the amount of difference diminishes until the two values become identical for F light. For G light α and β in the reverse positions differ by about 0.0001. This is in accordance with what was actually observed for C, Na, Tl, and F light.

The following (p. 373) is the table of refractive indices embodying the results of the measurements, confirmed as regards α by the above calculations.

The intermediate index β , reduced to a vacuum, may be expressed for any wave-length as far as F by the following general formula.

$$\beta = 1.4706 + \frac{679\,587}{\lambda^2} - \frac{4\,793\,400\,000\,600}{\lambda^4} + \dots\dots\dots$$

The α index is given by diminishing the β value by 0.0002 as far as C, 0.0001 between C and Tl, and is identical with β beyond this up to

F. The γ index is given by increasing the constant 1.4706 by 0.0058. This is thus an extreme case of positive double refraction, the α and β indices being so close together as to actually coincide for certain wave-lengths.

Determination of Refractive Indices of Cæsium Magnesium Sulphate.

Index.	Direction of vibrations.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 1 prism.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Mean refractive index.
α	Parallel 2nd median line lying in symmetry plane	Li	1.4833	1.4827	1.4823	—	1.4828
		C	1.4837	1.4831	1.4827	—	1.4832
		Na	1.4861	1.4856	1.4853	—	1.4857
		Tl	1.4883	1.4879	1.4877	—	1.4880
		F	1.4916	1.4913	1.4906	—	1.4912
	Parallel symmetry axis, b , now 2nd median line	G	1.4964	—	1.4950	1.4953	1.4956
β	Parallel symmetry axis, b	Li	1.4835	1.4829	1.4825	1.4830	1.4830
		C	1.4839	1.4833	1.4830	1.4834	1.4834
		Na	1.4862	1.4857	1.4854	1.4857	1.4858
		Tl	1.4885	1.4881	1.4879	1.4880	1.4881
		F	1.4917	1.4913	1.4906	1.4911	1.4912
	In symmetry plane at right angles to 1st median line	G	1.4962	—	1.4951	—	1.4957
γ	Parallel 1st median line c .	Li	1.4889	—	1.4887	1.4888	1.4888
		C	1.4893	—	1.4892	1.4892	1.4892
		Na	1.4916	—	1.4916	1.4915	1.4916
		Tl	1.4942	—	1.4940	1.4938	1.4940
		F	1.4972	—	1.4970	1.4969	1.4970
		G	1.5020	—	—	1.5011	1.5015

Alteration of Refraction by Increase of Temperature.—Measurements at 70° indicated that the indices are lowered by about 0.0016 by an increase of 50° in temperature. The prisms affording the values of α and β exhibit coincident images at 70° , even when examined with the high power eye-piece, as would be expected from the optic axial angle phenomena at this temperature. For wave-lengths beyond the green thallium line the α vibrations are parallel to the symmetry axis b and the β vibrations occur in the symmetry plane.

Ratios of Axes of Optical Velocity Ellipsoid.—These ratios calculated for sodium light are

$$\alpha : b : c = 1.0001 : 1 : 0.9961.$$

The closeness of the relative values of the first two axes is very clearly manifested by these ratios.

Molecular Optical Constants.—The following are the calculated values of these constants.

Axis of optical ellipsoid.....	α .	β .	γ .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \quad \cdot \cdot \quad \left\{ \begin{array}{l} \text{C.} \\ \text{G.} \end{array} \right.$	0·1071 0·1094	0·1071 0·1094	0·1082 0·1105
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \quad \left\{ \begin{array}{l} \text{C.} \\ \text{G.} \end{array} \right.$	63·11 64·49	63·15 64·50	63·78 65·14
Specific dispersion, $n_G - n_C$	0·0023	0·0023	0·0023
Molecular dispersion, $m_G - m_C$	1·38	1·35	1·36
Molecular refraction, $\frac{n - 1}{d} M$	C. 106·76	106·80	108·08

These values will be independent of temperature as the refraction diminishes with the density.

SALTS CONTAINING ZINC.

Potassium Zinc Sulphate, $K_2Zn(SO_4)_2 \cdot 6H_2O$.

There is a perfect *cleavage* parallel $r'\{\bar{2}01\}$, the cleaved surfaces affording sharp single images of the goniometer slit, at precisely 180° to the r' face present on each fragment.

Volume.

Relative Density.—The following four determinations were made.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4·1195	2·2399
3·7180	2·2426
4·6208	2·2402
4·3405	2·2426

Mean **2·2413**

Perrot obtained 2·245 at 16° ; Joule and Playfair gave 2·24.

Molecular Volume.— $\frac{M}{d} = \frac{443}{2·241} = 197·68$.

Distance Ratios.—The axial angle β was previously shown to be $75^\circ 12'$, and

$$a : b : c = 0·7413 : 1 : 0·5044.$$

Combining these with the molecular volume, the calculated distance ratios are

$$\chi : \psi : \omega = 6·0618 : 8·1773 : 4·1247.$$

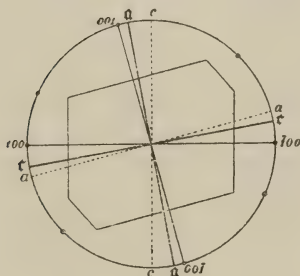
Optics.

Orientation of Axes of Optical Ellipsoid.—Two section-plates, ground parallel to the symmetry plane, exhibited the following ex-

tinction angles with respect to the normal to the basal plane $c\{001\}$, the direction being behind the normal nearer to the vertical axis c of the crystal, as indicated in Fig. 4.

Section 1	4° 40'
Section 2	4 20
Mean.. ...	<u>4 30</u>

FIG. 4.



Murmann and Rotter gave $4^\circ 43'$.

The axis of the optical ellipsoid nearly normal to the basal plane is again the second median line, and as the *sign of double refraction* is positive, this axis is a ; the direction of extinction at right angles to this in the symmetry plane is the minimum axis of the ellipsoid c , and is the first median line. The symmetry axis b is again the intermediate axis b . As the axial angle ac was shown in the former communication to be $75^\circ 12'$, the orientation of the axes is as follows.

The first median line t lies in the obtuse angle of the axes ac , and is inclined $4^\circ 30'$ to the axis a .

The second median line a lies also in the obtuse angle ac , and is inclined $10^\circ 18'$ to the vertical axis c .

The first median line is also inclined $85^\circ 30'$ to the normal to $c\{001\}$ and $10^\circ 18'$ to the normal to $a\{100\}$.

Optic Axial Angle.—The following measurements of the apparent angle in air were made with three excellent sections ground perpendicular to the first median line.

Determination of apparent Angle in Air of Potassium Zinc Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li.....	112° 14'	112° 24	112° 14'	112° 17'
C.....	112 16	112 26	112 16	112 19
Na.....	112 24	112 36	112 26	112 29
Tl.....	112 33	112 46	112 36	112 38
F.....	112 45	112 58	112 48	112 50

The angle given by Murmann and Rotter is $114^{\circ} 14'$, and by Perrot 114° .

Determination of true Optic Axial Angle of Potassium Zinc Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated value of 2Va.	Mean value of 2Va.
Li.....	{ 1 2 3	60° 11' 60 25 60 26	1a 2a 3a	95° 36' 95 46 95 40	68° 11' 68 18 68 21	68° 17'
C.....	{ 1 2 3	60 9 60 22 60 24	1a 2a 3a	95 34 95 42 95 39	68 10 68 17 68 20	
Na.....	{ 1 2 3	59 54 60 7 60 10	1a 2a 3a	95 12 95 18 95 18	68 8 68 15 68 18	
Th.....	{ 1 2 3	59 39 59 51 59 51	1a 2a 3a	94 47 94 53 94 46	68 6 68 13 68 16	68 12
F.....	{ 1 2 3	59 21 59 30 59 31	1a 2a 3a	94 20 94 20 94 16	68 3 68 10 68 13	

Monobromonaphthalene was the immersion liquid employed.

Very accurate measurement is required, using sections of sufficient thickness (2 or 3 mm.) to afford very small rings and fine brushes, in order to be certain of such a small amount of dispersion. A most valuable indication of the true order of dispersion of this salt is afforded by observations of the angle in turpentine and in toluene, whose refractive indices are only slightly lower and higher respectively than the mean refractive index of the crystal. As measured in toluene, the angle for red is indubitably larger than for blue, and by about $20'$. In turpentine scarcely any difference is perceptible. Hence the true angle is certainly largest for red light, and the order of dispersion given in the table is confirmed.

Murmann and Rotter give $69^{\circ} 5'$, without stating the order of dispersion. Perrot gives $69^{\circ} 3'$ for C, $68^{\circ} 20'$ for Na, and $68^{\circ} 37'$ for F, the tendency being for red to be greatest.

The angles calculated from the three refractive indices of the crystals are not trustworthy unless the indices are absolutely correct to the fourth decimal place, as shown in the communication concerning the simple sulphates. As this cannot be guaranteed, and in all probability the possible error amounts to 0.0002 after the most elaborate precautions, such calculations are useless for the purpose in view.

Dispersion of the Median Lines.—In turpentine, the optic axes both exhibit dispersion in the same direction, the hyperbolic brushes being

See errata
v. 69², p. 1756

fringed with colour in the following order, assuming the obtuse angle of the morphological axes, *ac*, to be on the left hand.

red | blue 1st M.L. red | blue.

The axes being dispersed inversely as the order of the fringes, the first median line is evidently slightly on the left of the central line for blue and on the right for red. As regards the relative amount of dispersion of each axis, there is no appreciable difference. In toluene, the axis on the left exhibits no coloured fringes, the other being as in turpentine; thus

no colour | no colour 1st M.L. red | blue.

Here again, however, the first median line for blue is evidently left of its position for red. Hence there can be no doubt that this represents the order of dispersion of the median lines. The true dispersion at each axis will be intermediate between the two cases, and nearer to the arrangement for toluene, whose refractive index is nearer the mean index of the crystal.

The first median line is consequently dispersed so as to lie a few minutes nearer to the crystallographic axes *a* for red than it does for blue, and the optic axis lying in the obtuse angle of the morphological axes *ac* is nearly coincident for all colours.

It is worth noticing the considerable difference between the indications as regards the latter optic axis in turpentine and in toluene, showing, as it does, how misleading the observations in either alone might be, and the care required in the choice of immersion liquids for this purpose.

Effect of rise of Temperature on the Optic Axial Angle.—Section 3 was heated to 90° and measurements of 2E were made at this temperature. The angle for sodium light was 115° 12'. Hence the optic axial angle increases nearly 3° for 70° rise of temperature.

Refractive Indices.—The results of the determinations of refractive index with six prisms ground upon five different crystals are given on p. 378; in the last column the values obtained by Perrot are given.

It is satisfactory to note the close agreement of Perrot's values with those now given. Murmann and Rotter give somewhat different values, for C they are α 1.476, β 1.480, and γ = 1.489; the γ value is particularly incorrect.

The mean refractive index of potassium zinc sulphate, corrected to a vacuum, is accurately expressed by the following formula for any wave-length λ as far as F.

$$\beta = 1.4690 + \frac{609\ 571}{\lambda^2} - \frac{3\ 444\ 700\ 000\ 000}{\lambda^4} + \dots\dots\dots$$

Determination of Refractive Indices of Potassium Zinc Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 1 prism.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Crystal 5, 1 prism.	Mean refrac- tive index.	Perrot's values.
α vibrations parallel 2nd median line α .	Li	1.4748	—	1.4750	1.4745	—	1.4748	—
	C	1.4752	—	1.4754	1.4749	—	1.4752	1.4749
	Na	1.4776	—	1.4777	1.4772	—	1.4775	1.4775
	Tl	1.4796	—	1.4801	1.4793	—	1.4797	—
	F	1.4826	—	1.4834	1.4819	—	1.4826	1.4826
	G	—	—	1.4870	1.4862	—	1.4866	—
β vibrations parallel symmetry axis b (b').	Li	1.4804	1.4805	1.4810	1.4802	1.4806	1.4805	—
	C	1.4808	1.4809	1.4814	1.4806	1.4810	1.4809	1.4811
	Na	1.4834	1.4832	1.4837	1.4829	1.4832	1.4833	1.4836
	Tl	1.4858	1.4857	1.4861	1.4853	1.4858	1.4857	—
	F	1.4892	1.4890	1.4894	1.4882	1.4886	1.4889	1.4888
	G	—	—	1.4936	1.4924	1.4926	1.4929	—
γ vibrations parallel 1st median line τ .	Li	—	1.4938	1.4939	—	1.4936	1.4938	—
	C	—	1.4942	1.4944	—	1.4940	1.4942	1.4940
	Na	—	1.4969	1.4972	—	1.4966	1.4969	1.4967
	Tl	—	1.4993	1.4996	—	1.4994	1.4994	—
	F	—	1.5026	1.5031	—	1.5023	1.5027	1.5024
	G	—	—	1.5072	—	1.5063	1.5067	—

As the dispersion differs appreciably for the three indices, the α and γ values are not so closely reproduced as usual by the same formula by diminishing and increasing the constant 1·4690 by fixed amounts; they are, however, on the average less and greater respectively than the β values by 0·0058 and 0·0136, the β indices being nearer to the α in accordance with the positive nature of the double refraction.

Alteration of Refraction by Rise of Temperature.—From measurements carried out at 70° with a pair of prisms, it appears that the indices are diminished by about 0·0018 for 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The calculated values of these ratios are

$$a : b : c = 1\cdot0039 : 1 : 0\cdot9909.$$

Molecular Optical Constants.—These are as follows—

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0·1258	0·1271	0·1301
	{ G. 0·1283	0·1298	0·1328
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$	{ C. 55·72	56·29	57·61
	{ G. 56·86	57·48	58·84
Specific dispersion, $n_G - n_C \dots$	0·0025	0·0027	0·0027
Molecular dispersion, $m_G - m_C \dots$	1·14	1·19	1·23
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 94·02	95·14	97·77

As rise of temperature affects density and refraction in like manner, these values will be independent of temperature.

Rubidium Zinc Sulphate, $Rb_2Zn(SO_4)_2 \cdot 6H_2O$.

There is a good cleavage parallel, $r'\{201\}$. The fractures were found to yield clear reflections of the goniometer signal at exactly 180° in each case to the remaining r' face.

Volume.

Relative Density.—The following are the results of four determinations of the density with different crops belonging to two entirely independent preparations, containing rubidium sulphate from the two different sources previously alluded to.

Weight of salt employed.	Sp. gr. at 20°/4°.
4·7593	2·5817
4·5051	2·5839
5·1428	2·5817
5·1740	2·5888

Mean 2·5840

Perrot obtained values ranging from 2.573 to 2.610, and gives the mean as 2.595.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{535.4}{2.584} = 207.2.$$

Distance Ratios.—It was shown in the former communication that the axial angle β is $74^\circ 7'$, and

$$a : b : c = 0.7373 : 1 : 0.5011.$$

Combining these with the molecular volume we obtain

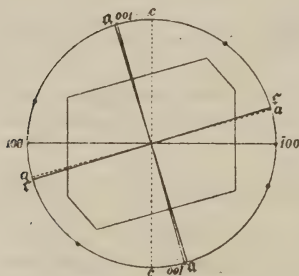
$$\chi : \psi : \omega = 6.1596 : 8.3543 : 4.1863.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—The extinctions on two sections parallel to the symmetry plane with respect to the normal to the basal plane were

Section 1	0° 40'
Section 2	1 0
Mean	0 50

FIG. 5.



The direction is forwards as shown in Fig. 5.

The axis of the optical ellipsoid which is nearly normal to $c\{001\}$ is again the second median line, and the axis at right angles to this in the symmetry plane is the first median line.

The *sign of double refraction* is positive, as usual for the series, a fact confirmed by the quarter undulation mica plate, and by the relations of the refractive indices. Hence the orientations may be stated as follows, having regard to the fact previously shown that the axial angle ac is $74^\circ 7'$.

The first median line t lies in the acute angle of the morphological axes ac , and makes an angle of $0^\circ 50'$ with the axis a .

The second median line a lies in the obtuse angle ac , and makes an angle of $16^\circ 43'$ with the vertical axis c .

The first median line is also inclined $90^\circ 50'$ to the normal to $c\{001\}$ and $16^\circ 43'$ to the normal to $a\{100\}$.

Perrot gives $90^\circ 30'$ as the inclination of the first median line to $\{001\}$.

Optic Axial Angle.—Three admirable pairs of plates were obtained by grinding, perpendicular to the first and second median lines. The angle in air is very large, and accurate measurements are only to be obtained with large and perfectly transparent sections. The following are the results.

Determination of the apparent Angle in Air of Rubidium Zinc Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$125^\circ 44'$	$125^\circ 34'$	$125^\circ 36'$	$125^\circ 38'$
C	125 45	125 35	125 38	125 39
Na	125 50	125 42	125 45	125 46
Tl	125 55	125 50	125 53	125 53
F	126 5	126 0	126 5	126 3

Perrot gives 128° for the angle in white light.

Determination of true Optic Axial Angle of Rubidium Zinc Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	1	$65^\circ 12'$	1a	$91^\circ 52'$	$73^\circ 44'$	73° 42'
	2	65 15	2a	92 1	73 42	
	3	65 8	3a	91 56	73 39	
C	1	65 7	1a	91 46	73 42	73 40
	2	65 11	2a	91 57	73 40	
	3	65 4	3a	91 50	73 38	
Na	1	64 38	1a	91 24	73 32	73 33
	2	64 46	2a	91 33	73 33	
	3	64 45	3a	91 29	73 34	
Tl.....	1	64 16	1a	91 1	73 24	73 27
	2	64 20	2a	91 5	73 26	
	3	64 25	3a	91 4	73 30	
F	1	63 42	1a	90 32	73 12	73 18
	2	63 45	2a	90 27	73 18	
	3	63 55	3a	90 30	73 24	

Monobromonaphthalene was employed as the immersion liquid.

Perrot indicates an optic axial angle of 74 — 75° .

Dispersion of the Median Lines.—The interference figure in toluene, whose index of refraction is identical with the mean index of the crystal, indicates that the optic axis which emerges between $a\{100\}$ and $r\{201\}$, is nearly coincident for all colours, whilst the other axis not far from normal to $r'\{201\}$ is dispersed about half a degree between Li and F, and for red is further removed from the crystal-

lographic axis a than for blue, which agrees with the amount of dispersion indicated in the above table of measurements. Hence the first median line is dispersed about $15'$ between Li and F, and lies for blue nearer to the crystallographic axis a than it does for red.

Effect of Rise of Temperature on Optic Axial Angle.—Section 1 was heated to 70° , and the angle for sodium light found to be $127^\circ 0'$. Hence the apparent angle in air increases about $1\frac{1}{4}^\circ$ for 50° rise of temperature.

Refractive Indices.—The following are the refractive indices, determined by means of six prisms ground upon four crystals.

Determination of Refractive Indices of Rubidium Zinc Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Mean refractive index.	Perrot's values.
α Vibs. par. 2nd median line α .	Li	—	1·4805	1·4809	1·4808	1·4807	—
	C	—	1·4809	1·4813	1·4812	1·4811	1·4806
	Na	—	1·4831	1·4835	1·4834	1·4833	1·4833
	Tl	—	1·4856	1·4859	1·4857	1·4857	—
	F	—	1·4884	1·4888	1·4887	1·4886	1·4883
	G	—	1·4929	—	—	1·4929	—
β Vibs. par. symmetry axis b (h)	Li	1·4855	1·4855	1·4858	1·4857	1·4856	—
	C	1·4859	1·4860	1·4862	1·4859	1·4860	1·4859
	Na	1·4882	1·4883	1·4888	1·4884	1·4884	1·4882
	Tl	1·4906	1·4907	1·4910	1·4908	1·4908	—
	F	1·4938	1·4936	1·4938	1·4940	1·4938	1·4942
	G	1·4981	1·4978	—	—	1·4980	—
γ Vibs. par. 1st median line γ	Li	1·4945	1·4948	1·4949	—	1·4947	—
	C	1·4949	1·4952	1·4953	—	1·4951	1·4945
	Na	1·4975	1·4976	1·4975	—	1·4975	1·4975
	Tl	1·5000	1·5002	1·5002	—	1·5001	—
	F	1·5031	1·5034	1·5033	—	1·5033	1·5030
	G	1·5078	1·5078	—	—	1·5078	—

The intermediate index β , corrected to a vacuum, is expressed for any wave-length λ as far as F by the formula

$$\beta = 1.4742 + \frac{602\ 511}{\lambda^2} - \frac{3\ 323\ 600\ 000\ 000}{\lambda^4} + \dots$$

The α indices are reproduced by the formula to within one or two units in the fourth decimal place if the constant 1·4742 is diminished by 0·0051, and the γ indices if it is increased by 0·0092. The smaller amount of the former difference determines the positive nature of the double refraction.

Alteration of Refraction by Increase of Temperature.—The indices

were determined upon two prisms at 70° , and found to be about 0.0012 lower at this temperature than the values above given.

Ratio of Axes of Optical Velocity Ellipsoid.—The values calculated from the refractive indices are as follows.

$$a : b : c = 1.0034 : 1 : 0.9939.$$

Molecular Optical Constants.—The calculated values of these constants are as under.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1102 G. 0.1125	0.1112 0.1135	0.1130 0.1154
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$			
Specific dispersion, $n_G - n_C$	0.0023	0.0023	0.0024
Molecular dispersion, $m_G - m_C$	1.23	1.25	1.31
Molecular refraction, $\frac{n - 1}{d} M$	C 99.77	100.78	102.67

These values will be independent of temperature, as the refraction has been shown to diminish as the temperature rises, and the density is similarly affected.

Cæsium Zinc Sulphate, $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

There is a well-defined *cleavage* parallel to the orthodome $r'\{201\}$. The cleaved surfaces afford sharp images of the goniometer signal at 180° in each case from the residual r' face.

Volume.

Relative Density.—The following four determinations were made with crystals belonging to different crops of the two independent preparations.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.4625	2.8668
5.1008	2.8707
3.6943	2.8652
3.5480	2.8652
Mean	<u>2.8670</u>

Perrot obtained numbers varying from 2.826 to 2.888, and ascribes 2.88 as the true density.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{630.4}{2.867} = 219.88.$$

Distance Ratios.—The axial angle ac was shown in the former communication to be $72^\circ 59'$, and the axial ratios

$$a : b : c = 0.7274 : 1 : 0.4960.$$

Combining these with the molecular volume, we find

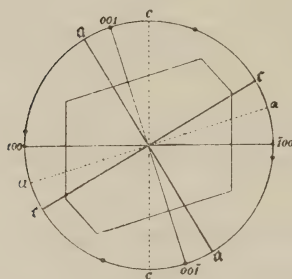
$$\chi : \psi : \omega = 6.2598 : 8.6058 : 4.2684.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—The extinctions on two section-plates ground parallel to the symmetry plane with respect to the normal to the basal plane were

Section 1	12° 50'
Section 2	13 40
Mean	<hr/> 13 15

FIG. 6.



The direction is forwards, as clearly represented in Fig. 6.

The axis near the normal to $c\{001\}$ is, as usual in the series, the second median line, the other axis of the optical ellipsoid which lies in the symmetry plane being the first median line.

A quarter undulation mica, and the relations of the three refractive indices, indicate a positive *sign of double refraction*, and with the knowledge of the axial angle ac , previously shown to be $72^\circ 59'$, the orientations work out as follows.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $13^\circ 15'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $30^\circ 16'$ to the vertical axis c .

The first median line is also inclined $103^\circ 15'$ to the normal to $c\{001\}$, and $30^\circ 16'$ to the normal to $a\{100\}$.

Perrot gives 112° as the inclination of first median line to $\{001\}$, a much larger angle than that exhibited by the author's crystals.

Optic Axial Angle.—The following measurements were obtained with three pairs of sections ground perpendicular to the first and second median lines. The angle in air is so large that only two of the sections exhibited it sufficiently clearly.

Determination of apparent Angle in Air of Cesium Zinc Sulphate.

Nature of light.	Section 1.	Section 2.	Mean 2E.
Li	131° 20'	131° 16'	131° 18'
C	131 10	131 10	131 10
Na	130 30	130 40	130 35
Tl	129 52	130 8	130 0
F	129 10	129 20	129 15

Determination of true Optic Axial Angle of Cesium Zinc Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	{ 1	66° 59'	1a	92° 45'	74° 38'	74° 30'
	{ 2	66 42	2a	92 55	74 22	
	{ 3	74 57	3a	106 14	74 31	
C	{ 1	66 55	1a	92 43	74 36	74 27
	{ 2	66 38	2a	92 52	74 20	
	{ 3	74 51	3a	106 18	74 26	
Na	{ 1	66 15	1a	92 24	74 16	74 11
	{ 2	66 1	2a	92 32	74 2	
	{ 3	74 37	3a	106 25	74 14	
Tl	{ 1	65 37	1a	92 12	73 53	73 52
	{ 2	65 33	2a	92 17	73 48	
	{ 3	74 11	3a	106 38	73 54	
F	{ 1	64 53	1a	91 55	73 28	73 31
	{ 2	64 55	2a	91 50	73 32	
	{ 3	73 50	3a	106 54	73 34	

The two first pairs of sections were measured in monobromonaphthalene, and the third pair in toluene, the results confirming each other admirably. Perrot gives for the angle 78° for white light, but it was not determined directly.

Dispersion of the Median Lines.—Additional observations of the interference figures were made in cedar oil ($\mu_D = 1.520$) and benzene ($\mu_D = 1.507$). The mean of the indices of toluene and cedar oil is approximately equal to the mean refractive index of the crystal, and the index of benzene is also about the same mean value. The phenomena in the latter liquid are consequently, and were actually observed to be, the mean of the phenomena exhibited in the two former liquids, and may be taken as representing the true character of the dispersion of the two optic axes, and hence of the first median line.

In benzene the two axial brushes are observed to be about equally fringed with colour in the following symmetrical order.

blue | red 1st M.L. red | blue

Moreover, the differences of the readings for red and blue light at

each axis were found to be each about 25'. Hence the median lines in this salt exhibit no appreciable dispersion.

Effect of Rise of Temperature on the Optic Axial Angle.—The apparent optic axial angle in air was determined at 70° with Section 1 in sodium light, and found to be 128°. Hence 2E decreases about $2\frac{1}{2}^\circ$ for 50° rise of temperature.

Refractive Indices.—The following are the results of the measurements with six prisms ground upon four different crystals.

Determination of Refractive Indices of Cesium Zinc Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.	Perrot's values.
α Vibs. par. 2nd median line α	Li	1·4993	1·4989	1·4999	—	1·4994	—
	C	1·4997	1·4993	1·5003	—	1·4998	1·4997
	Na	1·5022	1·5019	1·5026	—	1·5022	1·5020
	Tl	1·5046	1·5042	1·5053	—	1·5047	—
	F	1·5079	1·5076	1·5083	—	1·5079	1·5080
	G	1·5127	1·5123	1·5124	—	1·5125	—
β Vibs. par. symmetry axis b (β)	Li	1·5020	1·5016	—	1·5023	1·5020	—
	C	1·5024	1·5020	—	1·5027	1·5024	1·5025
	Na	1·5049	1·5045	—	1·5050	1·5048	1·5049
	Tl	1·5073	1·5069	—	1·5076	1·5073	—
	F	1·5105	1·5100	—	1·5107	1·5104	1·5107
	G	1·5154	1·5147	—	1·5153	1·5151	—
γ Vibs. par. 1st median line γ	Li	1·5063	1·5060	1·5068	1·5066	1·5064	—
	C	1·5067	1·5064	1·5073	1·5070	1·5068	1·5070
	Na	1·5092	1·5089	1·5098	1·5093	1·5093	1·5095
	Tl	1·5118	1·5114	1·5124	1·5120	1·5119	—
	F	1·5150	1·5147	1·5158	1·5153	1·5152	1·5154
	G	1·5199	1·5195	1·5203	1·5198	1·5199	—

The intermediate ~~axis~~ ^{index} β , reduced to a vacuum, is accurately represented as far as F, for any wave-length λ , by the formula

$$\beta = 1.4914 + \frac{539\ 594}{\lambda^2} - \frac{2\ 103\ 000\ 000\ 000}{\lambda^4} + \dots$$

The α indices are reproduced if the constant 1·4914 is diminished by 0·0026, and the γ values if it is increased by 0·0045. The former difference being the smaller, determines the positive nature of the double refraction.

Alteration of Refraction by Increase of Temperature.—Measurements with two of the prisms at 70° indicated that the indices are diminished about 0·0016 for 50° rise of temperature, the limits being 0·0013 to 0·0018

Ratio of Axes of Optical Velocity Ellipsoid.—The refractive indices lead to the following ratios.

$$a : b : c = 1.0017 : 1 : 0.9970.$$

Molecular Optical Constants.—These are as follows.

Axis of optical ellipsoid	α .	β .	γ .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$.	$\left\{ \begin{array}{l} \text{C. } 0.1026 \\ \text{G. } 0.1048 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1031 \\ 0.1053 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1038 \\ 0.1061 \end{array} \right.$
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	$\left\{ \begin{array}{l} \text{C. } 64.69 \\ \text{G. } 66.08 \end{array} \right.$	$\left\{ \begin{array}{l} 64.98 \\ 66.36 \end{array} \right.$	$\left\{ \begin{array}{l} 65.46 \\ 66.88 \end{array} \right.$
Specific dispersion, $n_G - n_C$	0.0022	0.0022	0.0023
Molecular dispersion, $m_G - m_C$	1.39	1.38	1.42
Molecular refraction $\frac{n - 1}{d} M$	C 109.98	110.56	111.52

These values are independent of temperature, refraction diminishing with density by rise of temperature.

SALTS CONTAINING IRON.

Potassium Ferrous Sulphate, $K_2Fe(SO_4)_2 \cdot 6H_2O$.

There is an excellent *cleavage* parallel to the orthodome $r'\{\bar{2}01\}$, as stated by Topsøe and Christiansen.

Volume.

Relative Density.—The following four determinations were made with different crops of clear crystals, freshly recrystallised and quite free from traces either of oxidation or efflorescence.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3.3358	2.1707
2.8228	2.1724
3.7412	2.1664
3.2737	2.1680

Mean 2.1694

Schiff gave 2.18 as the density of this salt.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{434}{2.169} = 200.09.$$

Distance Ratios.—The axial angle ac was previously shown to be $75^\circ 28'$, and the axial ratios

$$a : b : c = 0.7377 : 1 : 0.5020.$$

Combination of these with the molecular volume yields the following values for the distance ratios.

$$\chi : \psi : w = 6.0739 : 8.2336 : 4.1332.$$

The apparent angle in air is given by Murmann and Rotter as $111^{\circ} 56'$ for sodium light.

Determinations of true Optic Axial Angle of Potassium Ferrous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66^{\circ} 34' \\ 67 \ 45 \\ 66 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 111^{\circ} 36' \\ 114 \ 32 \\ 111 \ 46 \end{array} \right.$	$\left\{ \begin{array}{l} 67^{\circ} \ 8' \\ 67 \ 3 \\ 66 \ 52 \end{array} \right.$	$67^{\circ} \ 1'$
C.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \ 34 \\ 67 \ 45 \\ 66 \ 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 111 \ 34 \\ 114 \ 30 \\ 111 \ 44 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 9 \\ 67 \ 4 \\ 66 \ 53 \end{array} \right.$	$67 \ 2$
Na.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \ 37 \\ 67 \ 48 \\ 66 \ 19 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 111 \ 23 \\ 114 \ 24 \\ 111 \ 33 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 14 \\ 67 \ 8 \\ 66 \ 58 \end{array} \right.$	$67 \ 7$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \ 40 \\ 67 \ 51 \\ 66 \ 22 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 111 \ 12 \\ 114 \ 17 \\ 111 \ 23 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 20 \\ 67 \ 12 \\ 67 \ 4 \end{array} \right.$	$67 \ 12$
F.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \ 44 \\ 67 \ 55 \\ 66 \ 26 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 110 \ 54 \\ 114 \ 7 \\ 111 \ 6 \end{array} \right.$	$\left\{ \begin{array}{l} 67 \ 28 \\ 67 \ 18 \\ 67 \ 12 \end{array} \right.$	$67 \ 19$

The immersion liquid employed with the pairs 1 and 1a, 3 and 3a was toluene; in the case of 2 and 2a turpentine was used. One pair of sections (3 and 3a) were remeasured in monobromonaphthalene, and the values of 2Va obtained found to be practically identical with those obtained in toluene.

Murmann and Rotter found $68^{\circ} 4'$ for the true angle for sodium light, and Topsøe and Christiansen $67^{\circ} 18'$.

Dispersion of the Median Lines.—The observations of the interference figures in white light, in toluene and turpentine, whose indices of refraction are respectively higher and lower than the mean index of the crystals, together with a knowledge of the orientation of the sections during measurement of the optic axial angle in monochromatic light, and observations of the circle readings for each axis, indicate that the first median line is dispersed in such a manner that for Li light it lies nearer to the crystallographic axis *a* by about $10'$ than it does for F light. Both axes show dispersion, the one lying in the acute angle of the morphological axes *ac* only very slightly, as stated by Murmann and Rotter.

Effect of Rise of Temperature on the Optic Axial Angle.—The apparent angle in air was measured with Section 2 at 70° . The angle was found to be increased by about 2° for this rise of 50° of temperature. The section became opaque immediately after the reading was obtained, owing to decomposition.

Refractive Indices.—The following determinations were obtained with six prisms ground upon four different crystals.

Determination of Refractive Indices of Potassium Ferrous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.	Values of Topsøe and Christiansen.
α Vibs. par. 2nd median line	Li	1·4729	1·4733	1·4732	—	1·4731	—
	C	1·4732	1·4737	1·4736	—	1·4735	1·4751
	Na	1·4757	1·4760	1·4760	—	1·4759	1·4775
	Tl	1·4780	1·4782	1·4784	—	1·4782	—
	F	1·4810	1·4811	1·4812	—	1·4811	1·4833
	G	1·4852	—	—	—	1·4852	—
β Vibs. par. symmetry axis b (b)	Li	1·4792	1·4797	1·4796	1·4796	1·4795	—
	C	1·4796	1·4800	1·4800	1·4800	1·4799	1·4806
	Na	1·4820	1·4822	1·4823	1·4821	1·4821	1·4832
	Tl	1·4845	1·4847	1·4851	1·4846	1·4847	—
	F	1·4876	1·4878	1·4879	1·4877	1·4877	1·4890
	G	1·4917	—	—	1·4923	1·4920	—
γ Vibs. par. 1st median line ϵ	Li	1·4938	1·4943	—	1·4942	1·4941	—
	C	1·4942	1·4946	—	1·4946	1·4945	1·4947
	Na	1·4968	1·4970	—	1·4969	1·4969	1·4973
	Tl	1·4993	1·4997	—	1·4996	1·4995	—
	F	1·5025	1·5030	—	1·5030	1·5028	1·5041
	G	1·5067	—	—	1·5075	1·5071	—

Murmann and Rotter give the following values for β : for red 1·478, for yellow 1·480, for green 1·484, and for violet 1·489. The values obtained by Topsøe and Christiansen, of which only those for β were directly determined, are given in the last column, and differ considerably from the values now given.

The intermediate index β (in a vacuum) is represented, for any wave-length λ as far as F, by the following formula.

$$\beta = 1\cdot4728 + \frac{266\cdot439}{\lambda^2} + \frac{2\ 437\ 900\ 000\ 000}{\lambda^4} + \dots$$

The α values are closely reproduced by the formula if the constant 1·4728 is diminished by 0·0064, and the γ values if it is increased by 0·0147. The closer approximation of the α and β values than the β and γ values determines the positive nature of the double refraction.

Alteration of Refraction by Increase of Temperature.—The prisms were found incapable of withstanding a heat of 70° unimpaired, so the observations were limited to 55°. At this temperature the indices were about 0·0010 lower than at the ordinary temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The above indices of refraction furnish the following ratios.

$$a : b : c = 1.0042 : 1 : 0.9901.$$

Molecular Optical Constants.—Following are the calculated values of these constants.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1296	0.1310	0.1344
	{ G. 0.1323	0.1339	0.1373
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$	{ C. 56.22	56.87	58.34
	{ G. 57.41	58.09	59.60
Specific dispersion, $n_G - n_C$	0.0027	0.0029	0.0029
Molecular dispersion, $m_G - m_C$	1.19	1.22	1.26
Molecular refraction, $\frac{n - 1}{d} M$	C. 94.82	96.10	99.03

As refraction and density diminish together for rise of temperature, the above values are practically constant for all temperatures at which the salt is capable of existing.

Rubidium Ferrous Sulphate, $Rb_2Fe(SO_4)_2 \cdot 6H_2O$.

There is a perfect cleavage parallel $r'\{201\}$. The cleaved surfaces yield single images of the collimator slit of the goniometer, at 180° to the r' face left on each fragment.

Volume.

Relative Density.—The following four determinations were made with different crops.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.3513	2.5150
3.9436	2.5202
3.4670	2.5123
3.4734	2.5146

Mean 2.5155

Perrot gives the density at 15° as 2.51.

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{526.4}{2.516} = 209.22.$$

Distance Ratios.—The axial angle ac was given in the previous memoir as $74^\circ 16'$, and the ratio of the axes

$$a : b : c = 0.7377 : 1 : 0.5004.$$

Combination with the molecular volume affords the ratios

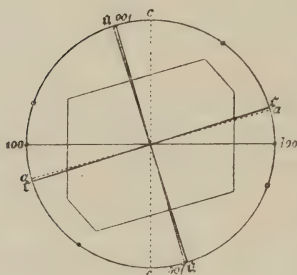
$$\chi : \psi : \omega = 6.1832 : 8.3817 : 4.1942.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Extinction in the symmetry plane occurs nearly normal and parallel to the basal plane $c\{001\}$. Two sections, ground parallel to the symmetry plane $b\{010\}$, afforded the following extinction angles with respect to the normal to $c\{001\}$.

Section 1	1° 55'
Section 2	0 55
Mean	<hr/> 1 25

FIG. 8.



The direction is forwards, as indicated in Fig. 8.

This axis is again the second median line, the direction at right angles in the symmetry plane being the first median line.

The *sign of double refraction* is, as usual in the series, positive, a fact demonstrated by use of the quarter undulation mica, and by the relations of the refractive indices.

As the axial angle ac is $74^{\circ} 16'$, the orientations are as under.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $1^{\circ} 25'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $17^{\circ} 9'$ to the vertical axis c .

The first median line is also inclined $91^{\circ} 25'$ to the normal to $c\{001\}$, and $17^{\circ} 9'$ to the normal to $a\{100\}$.

Perrot states that the first median line is inclined $91^{\circ} 30'$ to the normal to $\{001\}$, practically agreeing with the value now given.

Optic Axial Angle.—The following measurements were obtained with three pairs of section-plates ground perpendicular to the first and second median lines.

Determination of apparent Angle in Air of Rubidium Ferrous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li.....	125° 9'	124° 5'	124° 51'	124° 42'
C	125 16	124 12	124 58	124 49
Na.....	125 39	124 47	125 9	125 12
Tl.....	126 8	125 28	125 26	125 41
F	126 40	126 20	125 48	126 16

Determination of true Optic Axial Angle of Rubidium Ferrous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	{ 1	73° 5'	1a	105° 54'	73° 27'	73° 24'
	{ 2	73 2	2a	105 58	73 24	
	{ 3	64 48	3a	92 2	73 21	
C	{ 1	73 3	1a	105° 50'	73 27	73 23
	{ 2	73 0	2a	105 56	73 23	
	{ 3	64 44	3a	91 58	73 20	
Na.....	{ 1	72 56	1a	105 41	73 26	73 21
	{ 2	72 53	2a	105 47	73 21	
	{ 3	64 30	3a	91 44	73 16	
Tl.....	{ 1	72 48	1a	105 32	73 24	73 18
	{ 2	72 45	2a	105 40	73 19	
	{ 3	64 15	3a	91 30	73 11	
F	{ 1	72 35	1a	105 21	73 20	73 13
	{ 2	72 32	2a	105 29	73 14	
	{ 3	64 0	3a	91 16	73 6	

The immersion liquid was toluene for the first two pairs of sections, and monobromonaphthalene for the third pair.

The order of the colours fringing the hyperbolic brushes of the interference figures in toluene, using white light, confirms the order of dispersion; one brush was nearly colourless, that corresponding to the optic axis emerging between $a\{100\}$ and $r\{201\}$, whilst the other was clearly fringed with red on the side nearest the colourless brush and blue on the outer side, proving that the true angle for red is greater than the angle for blue. The fringes, when the observation is made in air, confirm the measured values, one brush being only very faintly coloured, while the other was brightly tinted red outside and blue within, proving that the apparent angle in air is greatest for blue.

Perrot estimated the true angle to be $73^\circ 2'$ for sodium light by observation with one plate in oil and utilisation of the medium index of refraction β of the crystal.

Dispersion of the Median Lines.—The phenomena and measurements in toluene prove that the first median line lies nearer to the morphological axis a for blue light than for red, the amount of dispersion between Li and F being about $10'$.

Effect of Rise of Temperature on the Optic Axial Angle.—One of the section-plates perpendicular to the first median line was examined at 70°, and the angle for sodium light was found to be 126° 0'. Hence the angle appears to increase about 1° for 50° rise of temperature.

Refractive Indices.—Six prisms were ground upon five different crystals. The results are given in the table, p. 395.

The β index in a vacuum is accurately expressed, for any wavelength λ as far as F, by the formula

$$\beta = 1.4747 + \frac{508\,396}{\lambda^2} - \frac{1\,863\,100\,000\,000}{\lambda^4} + \dots$$

The α indices are reproduced if the constant 1.4747 is diminished by 0.0059 and the γ values if it is increased by 0.0103. The smaller amount of the former difference again determines positive double refraction.

Alteration of Refraction by Rise of Temperature.—Determinations of refractive index at 60°, beyond which the observations cannot satisfactorily be carried on account of decomposition, indicate that at this temperature the indices are lower by about 0.0014 than they are at the ordinary temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices of refraction lead to the following ratios.

$$a : b : c = 1.0040 : 1 : 0.9931.$$

Molecular Optical Constants.—These are as under.

Axis of optical ellipsoid.....	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1128 G. 0.1153	0.1140 0.1164	0.1160 0.1186
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$			
Specific dispersion, $n_G - n_C \dots$	0.0025	0.0024	0.0026
Molecular dispersion, $m_G - m_C \dots$	1.30	1.28	1.32
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 100.36	101.58	103.71

These values will be substantially permanent for all temperatures at which the salt is capable of existence, as refraction and density vary together.

Cæsium Ferrous Sulphate, $\text{Cs}_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

There is a good *cleavage* parallel $r'\{201\}$. The cleaved surfaces were found to yield excellent images of the goniometer signal precisely at 180° to the r' face on the fragment examined.

Determination of Refractive Indices of Rubidium Ferrous Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 1 prism.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Crystal 5, 1 prism.	Mean refrac- tive index.	Perrot's values.
α vibrations parallel 2nd median line a.	Li	1.4792	1.4783	1.4795	1.4787	—	1.4789	—
	C	1.4795	1.4786	1.4799	1.4790	—	1.4793	1.4791
	Na	1.4818	1.4809	1.4821	1.4812	—	1.4815	1.4812
	Tl	1.4843	1.4832	1.4844	1.4837	—	1.4839	—
	F	1.4872	1.4865	1.4876	1.4867	—	1.4870	1.4868
	G	1.4916	—	—	—	—	1.4916	—
β vibrations parallel symmetry axis b (b).	Li	1.4849	—	1.4852	1.4845	1.4841	1.4847	—
	C	1.4854	—	1.4856	1.4848	1.4846	1.4851	1.4847
	Na	1.4877	—	1.4878	1.4870	1.4870	1.4874	1.4870
	Tl	1.4899	—	1.4903	1.4895	1.4893	1.4898	—
	F	1.4932	—	1.4932	1.4926	1.4925	1.4929	1.4926
	G	1.4975	—	—	—	1.4971	1.4973	—
γ vibrations parallel 1st median line c.	Li	—	1.4947	1.4954	—	1.4947	1.4949	—
	C	—	1.4950	1.4958	—	1.4950	1.4953	1.4953
	Na	—	1.4974	1.4981	—	1.4976	1.4977	1.4978
	Tl	—	1.5000	1.5008	—	1.5002	1.5003	—
	F	—	1.5033	1.5037	—	1.5033	1.5034	1.5036
	G	—	—	—	—	1.5080	1.5080	—

The *sign of double refraction* is again positive, as determined by the relations of the three refractive indices, and demonstrated by means of the quarter undulation mica.

The monoclinic angle being $73^{\circ} 8'$, the orientations are :

The first median line ϵ lies in the acute angle ac of the morphological axes, and is inclined $11^{\circ} 25'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $28^{\circ} 17'$ to the vertical axis c .

The first median line is also inclined $101^{\circ} 25'$ to the normal to $c\{001\}$ and $28^{\circ} 17'$ to the normal to $a\{100\}$.

Optic Axial Angle.—The apparent angle in air is very large and difficult to measure. Only one of the three section-plates, which were ground perpendicular to the first median line, afforded trustworthy readings. The mean angle obtained for sodium light was $132^{\circ} 47'$. The dispersion is very small, the angle being slightly larger for blue than for red, one of the brushes being almost free from colour when examined in white light, whilst the other is tinted blue on the side nearest the first median line and red outside.

Determination of the true Optic Axial Angle of Cæsium Ferrous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of $2H\alpha$.	No. of section perp. 2nd median line.	Observed values of $2H\sigma$.	Calculated values of $2V\alpha$.	Mean value of $2V\alpha$.
Li.....	{ 1	$67^{\circ} 10'$	$1a$	$92^{\circ} 5'$	$75^{\circ} 4'$	$75^{\circ} 2'$
	{ 2	$67^{\circ} 8$	$2a$	$92^{\circ} 10$	$75^{\circ} 1$	
	{ 3	$67^{\circ} 12$	$3a$	$92^{\circ} 20$	$75^{\circ} 0$	
C.....	{ 1	$67^{\circ} 4$	$1a$	$92^{\circ} 0$	$75^{\circ} 2$	$75^{\circ} 0$
	{ 2	$67^{\circ} 5$	$2a$	$92^{\circ} 7$	$75^{\circ} 0$	
	{ 3	$67^{\circ} 7$	$3a$	$92^{\circ} 15$	$74^{\circ} 58$	
Na.....	{ 1	$66^{\circ} 41$	$1a$	$91^{\circ} 45$	$74^{\circ} 52$	$74^{\circ} 51$
	{ 2	$66^{\circ} 45$	$2a$	$91^{\circ} 44$	$74^{\circ} 56$	
	{ 3	$66^{\circ} 42$	$3a$	$92^{\circ} 0$	$74^{\circ} 46$	
Tl.....	{ 1	$66^{\circ} 11$	$1a$	$91^{\circ} 25$	$74^{\circ} 40$	$74^{\circ} 42$
	{ 2	$66^{\circ} 20$	$2a$	$91^{\circ} 20$	$74^{\circ} 50$	
	{ 3	$66^{\circ} 17$	$3a$	$91^{\circ} 45$	$74^{\circ} 35$	
F.....	{ 1	$65^{\circ} 40$	$1a$	$90^{\circ} 58$	$74^{\circ} 30$	$74^{\circ} 31$
	{ 2	$65^{\circ} 50$	$2a$	$90^{\circ} 50$	$74^{\circ} 42$	
	{ 3	$65^{\circ} 40$	$3a$	$91^{\circ} 20$	$74^{\circ} 20$	

The three pairs of plates ground perpendicular to the first and second median lines were immersed in monobromonaphthalene for the determinations of $2H\alpha$ and $2H\sigma$. The order of dispersion was confirmed by observations of the interference figures afforded by the plates perpendicular to the first median line when immersed in benzene, whose refractive index is almost identical with the mean index of the crystal. The brushes were observed in white light to be

each fringed with red on the side nearest the first median line and blue outside, indicating a larger angle for red than for blue. Actual measurement showed a difference of $17'$ between C and Tl, confirming the above values.

Dispersion of the Median Lines.—The observations in benzene further showed that the axis emerging between $a\{100\}$ and $r\{201\}$ was slightly less dispersed than that on the other side of the median line, hence the first median line is nearer to the morphological axis a for blue than it is for red, the amount of difference being only a very few minutes.

Effect of Rise of Temperature on the Optic Axial Angle.—The section-plate which afforded the determination of $2E$ was heated to 70° , when the angle for sodium light was found to be $131^\circ 20'$. Hence the apparent angle in air diminishes about $1\frac{1}{2}^\circ$ for 50° rise of temperature.

Refractive Indices.—These were determined by means of six prisms ground upon four different crystals. The results are as follows.

Determination of Refractive Indices of Cæsium Ferrous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.
α Vibrations parallel 2nd median line α .	Li	1·4977	1·4973	1·4978	1·4976	1·4976
	C	1·4981	1·4977	1·4981	1·4981	1·4980
	Na	1·5004	1·5001	1·5005	1·5002	1·5003
	Tl	1·5031	1·5026	1·5028	1·5026	1·5028
	F	1·5062	1·5057	1·5063	1·5061	1·5061
	G	1·5107	1·5103	—	1·5104	1·5105
β Vibrations parallel symmetry axis b (h).	Li	1·5009	1·5005	1·5008	—	1·5007
	C	1·5013	1·5009	1·5011	—	1·5011
	Na	1·5035	1·5035	1·5036	—	1·5035
	Tl	1·5061	1·5060	1·5063	—	1·5061
	F	1·5092	1·5093	1·5094	—	1·5093
	G	1·5135	1·5140	—	—	1·5137
γ Vibrations parallel 1st median line γ .	Li	1·5070	1·5061	—	1·5065	1·5065
	C	1·5074	1·5065	—	1·5069	1·5069
	Na	1·5098	1·5090	—	1·5093	1·5094
	Tl	1·5125	1·5117	—	1·5120	1·5121
	F	1·5159	1·5148	—	1·5153	1·5153
	G	1·5203	1·5193	—	1·5198	1·5198

The β index reduced to a vacuum is accurately represented, for any wave-length λ as far as F, by the formula

$$\beta = 1.4911 + \frac{462\ 915}{\lambda^2} - \frac{645\ 800\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced if the constant 1.4911 is diminished by 0.0032 and the γ values if it is increased by 0.0059. The smaller amount of the former difference determines the positive nature of the double refraction.

Alteration of Refraction by Rise of Temperature.—Determinations of refractive index were made at 70°, and the mean results indicate that the indices are lower at this temperature by about 0.0017 than they are at the ordinary temperature. The prisms appeared capable of withstanding this temperature for some little time before opacity ensued, affording another indication of the greater stability of the cæsium salts than those of rubidium and potassium.

Ratio of Axes of Optical Velocity Ellipsoid.—The foregoing refractive indices afford the following ratios.

$$a : b : c = 1.0021 : 1 : 0.9961.$$

Molecular Optical Constants.—The calculated values of these constants are as under.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1051	0.1057	0.1067
	{ G. 0.1073	0.1079	0.1090
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C. 65.31	65.65	66.29
	{ G. 66.69	67.04	67.71
Specific dispersion, $n_G - n_C$	0.0022	0.0022	0.0023
Molecular dispersion, $m_G - m_C$	1.38	1.39	1.42
Molecular refraction, $\frac{n - 1}{d} M$	C. 111.01	111.70	112.99

These values will be sensibly constant for all temperatures at which the salt is able to exist, as refraction and density are altered in the same direction by change of temperature.

SALTS CONTAINING MANGANESE.

Further efforts to prepare the potassium salt of this group have been unavailing.

Rubidium Manganous Sulphate, $Rb_2Mn(SO_4)_2 \cdot 6H_2O$.

An excellent *cleavage* is developed parallel $r'\{201\}$; the cleaved surfaces exhibit sharply defined images of the goniometer signal at 180° to the r' face left on each fragment.

Volume.

Relative Density.—The following four determinations were carried out with different crops of clear crystals.

Weight of salt employed.	Sp. gr. at 26°/4°.
5.6872	2.4542
4.5172	2.4561
4.3798	2.4637
4.2636	2.4618

Mean 2.4590

Perrot gives the density at 15° as 2.49.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{525.4}{2.459} = 213.66.$$

Distance Ratios.—The axial angle having been shown to be $74^{\circ} 3'$, and the axial ratio

$$a : b : c = 0.7382 : 1 : 0.4950,$$

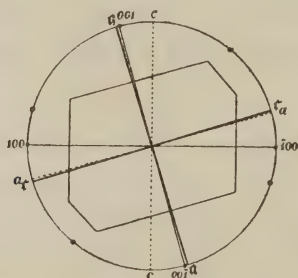
the distance ratios obtained by combination of these constants with the molecular volume are

$$\chi : \psi : \omega = 6.2542 : 8.4723 : 4.1938.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Some difficulty was experienced in determining the extinction angle in the symmetry plane by means of sections ground parallel to that plane, on account of slight surface alteration which interfered with the sharpness of the extinction. Four section-plates were ground as rapidly as possible consistent with due care, but only approximate determinations of extinction could be carried out with each. The mean, however, is probably very near the truth, and was $1^{\circ} 0'$ forward from the normal to $c\{001\}$ as shown in Fig. 10, the limits being about a degree each side of this position.

FIG. 10.



This direction is again the second median line, the other axis of the optical ellipsoid at right angles to this in the symmetry plane being the first median line.

The sign of double refraction is likewise positive, a fact which was

proved by means of the quarter undulation mica, and by the mutual relations of the three refractive indices.

The axial angle being $74^{\circ} 3'$, the orientations may be stated as follows.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $1^{\circ} 0'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $16^{\circ} 57'$ to the vertical axis c .

The first median line is also inclined $91^{\circ} 0'$ to the normal to $c\{001\}$ and $16^{\circ} 57'$ to the normal to $a\{100\}$.

Perrot gives the inclination to $\{001\}$ as $91^{\circ} 20'$.

Optic Axial Angle.—The following determinations were carried out with three pairs of section-plates ground perpendicular to the first and second median lines. They afforded clear interference figures, the surface alteration so inconvenient for the determinations of extinction being too slight to materially affect the interference figures when the sections were freshly prepared.

Determination of apparent Angle in Air of Rubidium Manganous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$109^{\circ} 40'$	$109^{\circ} 50'$	$109^{\circ} 48'$	$109^{\circ} 46'$
C	109 42	109 52	109 52	109 49
Na	109 52	110 0	110 0	109 57
Tl	110 3	110 10	110 8	110 7
F	110 22	110 18	110 17	110 19

Determination of true Optic Axial Angle of Rubidium Manganous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of $2H\alpha$.	No. of section perp. 2nd median line.	Observed values of $2Ho$.	Calculated values of $2Va$.	Mean value of $2Va$.
Li	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 59^{\circ} 12' \\ 59 27 \\ 59 15 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 96^{\circ} 21' \\ 96 20 \\ 96 20 \end{array} \right.$	$\left\{ \begin{array}{l} 67^{\circ} 4' \\ 67 17 \\ 67 8 \end{array} \right.$	$67^{\circ} 10'$
C	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 59 8 \\ 59 21 \\ 59 10 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 96 18 \\ 96 13 \\ 96 15 \end{array} \right.$	$\left\{ \begin{array}{l} 67 3 \\ 67 15 \\ 67 6 \end{array} \right.$	67 8
Na	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 58 54 \\ 59 0 \\ 58 58 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 95 52 \\ 95 53 \\ 95 54 \end{array} \right.$	$\left\{ \begin{array}{l} 67 2 \\ 67 8 \\ 67 4 \end{array} \right.$	67 5
Tl	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 58 40 \\ 58 38 \\ 58 40 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 95 27 \\ 95 26 \\ 95 27 \end{array} \right.$	$\left\{ \begin{array}{l} 67 1 \\ 67 0 \\ 67 1 \end{array} \right.$	67 1
F	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 58 20 \\ 58 10 \\ 58 15 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 94 55 \\ 94 55 \\ 94 50 \end{array} \right.$	$\left\{ \begin{array}{l} 66 58 \\ 66 50 \\ 66 56 \end{array} \right.$	66 55

Monobromonaphthalene was the immersion liquid employed in the

measurements of 2Ha and 2Ho. The order of dispersion was confirmed by observation in white light of 2Ha in turpentine. Whilst one optic axial brush was almost free from a trace of colour, the other was brightly tinted red inside nearest the first median line, and blue outside, thus indicating a larger angle for red than for blue. An observation in toluene afforded confirmatory evidence. Perrot gives $67^{\circ} 38'$ for the angle in yellow light, deduced from an observation with one plate in oil.

Dispersion of the Median Lines.—In conducting the observation in turpentine the position of the section was carefully noted with reference to the crystal faces upon its broad edges, and it was found that the immovable optic axis was the one which emerges between $a\{100\}$ and $r\{201\}$, hence the first median line is dispersed in such a manner that for blue light it lies nearer by about $10'$ to the morphological axis a than it does for red.

Effect of Rise of Temperature on the Optic Axial Angle.—One of the section-plates perpendicular to the first median line was heated to 70° , at which temperature the angle for sodium light was found to be $110^{\circ} 50'$. Hence the apparent angle in air increases about a degree for 50° rise of temperature.

Refractive Indices.—Six prisms were employed, ground upon four different crystals. The following table represents the results.

Determination of Refractive Indices of Rubidium Manganous Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Mean refractive index.	Perrot's values.
α Vibs. par. 2nd median line α	Li	—	1·4737	1·4741	1·4746	1·4741	—
	C	—	1·4741	1·4745	1·4749	1·4745	1·4741
	Na	—	1·4764	1·4767	1·4770	1·4767	1·4764
	Tl	—	1·4787	1·4791	1·4796	1·4791	—
	F	—	1·4814	1·4823	1·4826	1·4821	1·4818
	G	—	1·4859	—	1·4868	1·4864	—
β Vibs. par. symmetry axis b (b)	Li	1·4770	1·4782	1·4784	1·4788	1·4781	—
	C	1·4775	1·4787	1·4787	1·4792	1·4785	1·4785
	Na	1·4797	1·4807	1·4809	1·4816	1·4807	1·4809
	Tl	1·4818	1·4833	1·4835	1·4839	1·4831	—
	F	1·4850	1·4860	1·4863	1·4869	1·4860	1·4864
	G	—	1·4901	1·4910	1·4910	1·4907	—
γ Vibs. par. 1st median line γ	Li	1·4872	1·4882	1·4886	—	1·4880	—
	C	1·4877	1·4887	1·4889	—	1·4884	1·4886
	Na	1·4899	1·4910	1·4911	—	1·4907	1·4910
	Tl	1·4926	1·4935	1·4939	—	1·4933	—
	F	1·4958	1·4969	1·4967	—	1·4965	1·4970
	G	—	1·5012	1·5019	—	1·5015	—

The β index reduced to a vacuum is accurately represented, for any wave-length λ as far as F, by the formula

$$\beta = 1.4694 + \frac{420\ 367}{\lambda^2} - \frac{491\ 200\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced by the formula if the constant 1.4694 is diminished by 0.0040 and the γ values if it is increased by 0.0100. The positive nature of the double refraction is evident from the smaller amount of the former difference from β .

Effect of Rise of Temperature on Refraction.—The indices were determined at 70°, and found to be about 0.0018 less at this temperature than the numbers given in the preceding table.

Ratio of Axes of Optical Velocity Ellipsoid.—The foregoing refractive indices lead to the following ratios.

$$a : b : c = 1.0027 : 1 : 0.9933.$$

Molecular Optical Constants.—The indices also afford the following constants when combined with the density and molecular weight.

Axis of optical ellipsoid	a .	b .	c .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1145 G. 0.1169	0.1153 0.1178	0.1173 0.1200
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$			
Specific dispersion, $n_G - n_C \dots$	0.0024	0.0025	0.0027
Molecular dispersion, $m_G - m_C \dots$	1.29	1.31	1.39
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 101.47	102.32	104.44

As in the case of the salts previously described, refraction and density vary together for change of temperature, and therefore the above constants will remain sensibly constant for all variations of temperature within whose limits the crystallised substance is capable of existing.

Cæsium Manganous Sulphate, Cs₂Mn(SO₄)₂.6H₂O.

In addition to the faces described in the previous memoir as being observed upon the crystals of this salt, many of the crystals specially prepared for the optical work exhibited well-defined small faces of the primary hemipyramid $\sigma\{111\}$ —P.

There is a perfect cleavage parallel $r'\{\bar{2}01\}$. The fractured surfaces afford sharp single images of the goniometer signal, and at precisely 180° to the r' face left on each fragment.

Volume.

Relative Density.—Four determinations with different crops of perfectly clear, transparent crystals yielded the following results.

Weight of salt employed.	Sp. gr. at 20°/4°.
4.4329	2.7365
4.4677	2.7393
3.2177	2.7385
2.4249	2.7356

Mean 2.7375

$$\text{Molecular Volume.} - \frac{M}{d} = \frac{620.4}{2.738} = 226.59.$$

Distance Ratios.—Combining the above molecular volume with the morphological constants given in the previous memoir, $\beta = 72^\circ 53'$ and

$$a : b : c = 0.7274 : 1 : 0.4913,$$

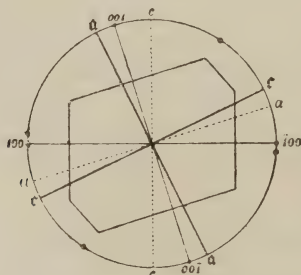
we obtain for the distance ratios the following values.

$$\chi : \psi : \omega = 6.3441 : 8.7217 : 4.2850.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Two excellent sections were obtained by grinding, parallel to the symmetry plane $b\{010\}$, exhibiting no tendency to deterioration as in case of rubidium mangano sulphate. The extinction angles afforded by them with respect to the normal to $c\{001\}$ were in each case precisely $8^\circ 20'$, the direction being forwards, as indicated in Fig. 11.

FIG. 11.



This direction is the second median line, and the first median line is, as usual in the series, perpendicular to it in the symmetry plane.

The *sign of double refraction* is positive, determined as in the cases of the salts previously described. As the morphological axial angle ac is $72^\circ 53'$, the orientations are as under.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $8^\circ 20'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $25^\circ 27'$ to the vertical axis c .

The first median line is likewise inclined $98^{\circ} 20'$ to the normal to $c\{001\}$, and $25^{\circ} 27'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Three pairs of sections afforded the following values.

Determination of apparent Angle in Air of Cæsium Manganous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$97^{\circ} 26'$	$97^{\circ} 20'$	$97^{\circ} 21'$	$97^{\circ} 22'$
C	$97 21$	$97 15$	$97 17$	$97 18$
Na	$97 1$	$96 54$	$96 55$	$96 57$
Tl	$96 41$	$96 28$	$96 30$	$96 33$
F	$96 10$	$95 54$	$95 55$	$96 0$

Determination of true Optic Axial Angle of Cæsium Manganous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 53^{\circ} 48' \\ 53 49 \\ 54 0 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 102^{\circ} 55' \\ 102 46 \\ 102 59 \end{array} \right.$	$\left\{ \begin{array}{l} 60^{\circ} 6' \\ 60 10 \\ 60 15 \end{array} \right.$	$60^{\circ} 10'$
C	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 53 43 \\ 53 42 \\ 53 56 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 102 50 \\ 102 42 \\ 102 55 \end{array} \right.$	$\left\{ \begin{array}{l} 60 3 \\ 60 5 \\ 60 12 \end{array} \right.$	$60 7$
Na	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 53 26 \\ 53 21 \\ 53 38 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 102 33 \\ 102 21 \\ 102 36 \end{array} \right.$	$\left\{ \begin{array}{l} 59 54 \\ 59 54 \\ 60 4 \end{array} \right.$	$59 57$
Tl	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 53 5 \\ 52 57 \\ 53 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 102 13 \\ 102 0 \\ 102 12 \end{array} \right.$	$\left\{ \begin{array}{l} 59 44 \\ 59 41 \\ 59 53 \end{array} \right.$	$59 46$
F	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 52 30 \\ 52 30 \\ 52 45 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 101 50 \\ 101 35 \\ 101 40 \end{array} \right.$	$\left\{ \begin{array}{l} 59 21 \\ 59 26 \\ 59 38 \end{array} \right.$	$59 28$

The immersion liquid was monobromonaphthalene in each determination of 2Ha and 2Ho. The order of dispersion was confirmed by observation of the interference figures in white light afforded by the sections perpendicular to the first median line, both in toluene and in cedar oil, the mean of whose refractive indices is near the mean index of the crystal.

Dispersion of the Median Lines.—The observations in toluene and cedar oil in white and in monochromatic light indicate that the optic axis which emerges not far from normal to $a\{100\}$ is only slightly dispersed, for blue being nearest to the first median line, whilst the other axis exhibits considerable dispersion, being again for blue nearest the median line. Hence the first median line is dispersed so that for blue it lies nearer to the morphological axis a than for red,

the amount indicated by the observations in monochromatic light being about 15' between Li and F.

Effect of Rise of Temperature on the Optic Axial Angle.—Section 1 was heated to 70°, and at this temperature the apparent angle in air measured 94° 35' for sodium light. Hence 2E diminishes about 2½° for 50° rise of temperature.

Refractive Indices.—The following values were obtained from six prisms ground upon three different crystals.

Determination of Refractive Indices of Cæsium Manganous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Mean refractive index.
α Vibrations parallel 2nd median line a	Li	1·4919	1·4920	1·4916	1·4918
	C	1·4923	1·4923	1·4919	1·4922
	Na	1·4948	1·4947	1·4944	1·4946
	Tl	1·4974	1·4972	1·4970	1·4972
	F	1·5006	1·5003	1·5000	1·5003
	G	1·5050	1·5046	1·5041	1·5046
β Vibrations parallel symmetry axis b (b)	Li	1·4933	1·4938	1·4937	1·4936
	C	1·4938	1·4942	1·4941	1·4940
	Na	1·4962	1·4968	1·4968	1·4966
	Tl	1·4988	1·4991	1·4993	1·4991
	F	1·5020	1·5022	1·5023	1·5022
	G	1·5064	1·5066	1·5068	1·5066
γ Vibrations parallel 1st median line c .	Li	1·4994	1·4997	1·4995	1·4995
	C	1·4998	1·5001	1·4999	1·4999
	Na	1·5025	1·5027	1·5024	1·5025
	Tl	1·5050	1·5052	1·5051	1·5051
	F	1·5082	1·5084	1·5083	1·5083
	G	1·5128	1·5130	1·5128	1·5129

The intermediate axis β in a vacuum is expressed, for any wavelength λ as far as F, by the formula

$$\beta = 1\cdot4803 + \frac{722\ 115}{\lambda^2} - \frac{4\ 944\ 600\ 000\ 000}{\lambda^4} + \dots$$

The α indices are reproduced very closely if the constant 1·4803 is diminished by 0·0019, and the γ indices if the constant is increased by 0·0059. The former being the smaller difference, determines the positive nature of the double refraction.

Effect of Rise of Temperature on Refraction.—The indices afforded by determinations at 70° indicate a lowering of about 0·0018 by 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The foregoing refractive indices yield the following ratios.

$$a : b : c = 1\cdot0013 : 1 : 0\cdot9961.$$

Molecular Optical Constants.—Beneath are given the calculated values of these constants.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0·1061	0·1064	0·1075
	{ G. 0·1083	0·1087	0·1098
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$	{ C. 65·81	66·01	66·68
	{ G. 67·21	67·43	68·14
Specific dispersion, $n_G - n_C$	0·0022	0·0023	0·0023
Molecular dispersion, $m_G - m_C$	1·40	1·42	1·45
Molecular refraction, $\frac{n - 1}{d} M$	C. 111·62	112·03	113·36

These values are again practically independent of temperature, as the refraction diminishes along with the density on increase of temperature.

SALTS CONTAINING NICKEL.

Potassium Nickelous Sulphate, $K_2Ni(SO_4)_2 \cdot 6H_2O$.

The crystals exhibit a perfect *cleavage* parallel to $r'\{201\}$. The fractures yield clearly defined single images of the goniometer signal at exactly 180° in each case from the r' face left on the fragment.

Volume.

Relative Density.—Four determinations were made with excellent crystals of different crops belonging to two independent preparations. The numbers obtained were as under.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3·1592	2·2305
3·0850	2·2344
4·2979	2·2314
4·5574	2·2357

Mean **2·2330**

The value of Kopp, 2·123, quoted by Perrot, is certainly incorrect.

Molecular Volume.— $\frac{M}{d} = \frac{436·9}{2·233} = 195·65$.

Distance Ratios.—The data given in the previous memoir, $\beta = 75^\circ 0'$ and

$$a : b : c = 0·7379 : 1 : 0·5020,$$

when combined with the molecular volume, afford the following distance ratios.

$$\chi : \psi : w = 6·0342 : 8·1775 : 4·1051.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Three sections were

Determination of apparent Angle in Air of Potassium Nickelous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	130° 15'	130° 30'	130° 10'	130° 18'
C	130 20	130 35	130 15	130 23
Na.....	131 2	131 5	130 45	130 57
Tl	131 42	131 40	131 20	131 34
F.....	132 30	132 22	132 14	132 22

Murmann and Rotter state that the apparent angle in air is less for red than for blue, which agrees with the above, and give 131° 45' as the angle, presumably for sodium light.

Determination of true Optic Axial Angle of Potassium Nickelous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66^{\circ} 50' \\ 67 0 \\ 66 50 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 91^{\circ} 0' \\ 91 15 \\ 91 4 \end{array} \right.$	$\left\{ \begin{array}{l} 75^{\circ} 21' \\ 75 22 \\ 75 19 \end{array} \right.$	$\left. \right\} 75^{\circ} 21'$
C	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 43 \\ 66 53 \\ 66 45 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 90 52 \\ 91 7 \\ 90 58 \end{array} \right.$	$\left\{ \begin{array}{l} 75 20 \\ 75 20 \\ 75 18 \end{array} \right.$	$\left. \right\} 75 19$
Na.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 22 \\ 66 32 \\ 66 25 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 90 27 \\ 90 42 \\ 90 35 \end{array} \right.$	$\left\{ \begin{array}{l} 75 16 \\ 75 16 \\ 75 16 \end{array} \right.$	$\left. \right\} 75 16$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 1 \\ 66 11 \\ 66 6 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 90 0 \\ 90 15 \\ 90 5 \end{array} \right.$	$\left\{ \begin{array}{l} 75 13 \\ 75 13 \\ 75 14 \end{array} \right.$	$\left. \right\} 75 13$
F	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 65 30 \\ 65 40 \\ 65 40 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 89 24 \\ 89 39 \\ 89 30 \end{array} \right.$	$\left\{ \begin{array}{l} 75 8 \\ 75 8 \\ 75 12 \end{array} \right.$	$\left. \right\} 75 9$

The immersion liquid employed was monobromonaphthalene.

The order of dispersion was confirmed by observations in toluene, whose refractive index is exactly the same for sodium light as the β index of the crystal, and only very slightly less than the mean index of the crystal; also in benzene whose index is slightly higher than the mean index of the crystal. In both cases the angle for red was clearly larger than for blue.

Murmann and Rotter represent the true optic axial angle as 75° 36'.

Dispersion of the Median Lines.—The observations in toluene and benzene indicated that the optic axis which emerges nearly perpendicular to the possible face $r\{201\}$ remains almost constant for all colours, whilst the other axis which emerges nearly normal to $r'\{201\}$ is clearly dispersed, being nearer to the stationary axis for blue than

for red. Hence the first median line is dispersed so that it lies nearer to the morphological axis a for red than it does for blue, the amount indicated in toluene being about $10'$ between Li and F. This order of dispersion of the median lines agrees with the observation of Murmann and Rotter, but the dispersion of the axes is the inverse. The observations above given were repeated and confirmed with each of the three sections.

Effect of Rise of Temperature on the Optic Axial Angle.—Section 3 was heated to 70° , and the angle for sodium light found to be $133^\circ 25'$. Hence the apparent angle in air increases by about $2\frac{1}{2}^\circ$ for 50° rise of temperature.

Refractive Indices.—The following table represents the results obtained with six prisms, ground upon four different crystals.

Determination of Refractive Indices of Potassium Nickelous Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Mean refractive index.
α Vibrations parallel 2nd median line a .	Li	—	1·4809	1·4807	1·4812	1·4809
	C	—	1·4813	1·4812	1·4815	1·4813
	Na	—	1·4836	1·4834	1·4839	1·4836
	Tl	—	1·4861	1·4857	1·4862	1·4860
	F	—	1·4889	1·4886	1·4893	1·4889
	G	—	1·4933	1·4931	1·4934	1·4933
β Vibrations parallel symmetry axis b b	Li	1·4888	1·4889	1·4889	1·4889	1·4889
	C	1·4892	1·4893	1·4895	1·4893	1·4893
	Na	1·4915	1·4914	1·4919	1·4917	1·4916
	Tl	1·4938	1·4941	1·4942	1·4942	1·4941
	F	1·4970	1·4971	1·4974	1·4973	1·4972
	G	1·5014	1·5015	1·5017	1·5013	1·5015
γ Vibrations parallel 1st median line c	Li	1·5024	1·5025	1·5017	—	1·5022
	C	1·5028	1·5029	1·5021	—	1·5026
	Na	1·5053	1·5052	1·5049	—	1·5051
	Tl	1·5077	1·5078	1·5075	—	1·5077
	F	1·5111	1·5110	1·5107	—	1·5109
	G	1·5155	1·5154	1·5151	—	1·5153

There was a considerable amount of absorption at the red end of the spectrum produced by each of the prisms, but the lime-light afforded ample illumination of the refracted images of the spectrometer slit for Li and C light, even when the openings of the receiving and exit slits of the monochromatic illuminator were as fine as usual.

Three rough values of the indices for the middle portion of the spectrum are given by Murmann and Rotter, $\alpha = 1·483$, $\beta = 1·490$, and $\gamma = 1·502$; they also state that β for red = $1·487$, for yellow = $1·489$, for green = $1·492$, and for violet = $1·495$.

The intermediate index β , in a vacuum, is accurately expressed, for any wave-length λ as far as F, by the formula

$$\beta = 1.4798 + \frac{437\ 765}{\lambda^2} - \frac{496\ 200\ 000\ 000}{\lambda^4} + \dots$$

The α index is closely reproduced by the formula if the constant 1.4798 is diminished by 0.0080, and the γ values if it is increased by 0.0135. The positive nature of the double refraction is evident from the fact that the former is the smaller difference from β .

Effect of Rise of Temperature on Refraction.—The indices were found to be lower by about 0.0012 at 70° than they are at the ordinary temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The refractive indices furnish the following ratios.

$$a : b : c = 1.0054 : 1 : 0.9910.$$

Molecular Optical Constants.—The calculated values of these constants are given below.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1276 G. 0.1303	{ 0.1294 0.1321	{ 0.1324 0.1352
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$			
Specific dispersion, $n_G - n_C \dots$	0.0027	0.0027	0.0028
Molecular dispersion, $m_G - m_C \dots$	1.18	1.19	1.22
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 94.25	95.81	98.42

As refraction and density vary together with change of temperature, these values will be independent of temperature.

Rubidium Nickelous Sulphate, Rb₂Ni(SO₄)₂·6H₂O.

The crystals of this salt exhibit a perfect *cleavage* parallel to $r'\{201\}$, in common with the other salts of the series. It was proved to be exactly 180° from r' by goniometrical measurement, the fractures yielding sharp images.

Volume.

Relative Density.—The following four determinations were made with beautifully clear crystals of this salt, derived from different crops.

Weight of salt employed.	Sp. gr. at 20°/4°.
5.1109	2.5817
4.4324	2.5833
3.8084	2.5807
3.5480	2.5848

Mean 2.5826

Perrot attributes a density of 2.56 to the salt.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{529.3}{2.583} = 204.92.$$

Distance Ratios.—The axial angle ac being $73^\circ 57'$, and the axial ratio

$$a : b : c = 0.7350 : 1 : 0.5022,$$

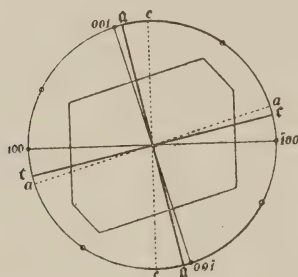
as previously given, the distance ratios obtained by combination with the molecular volume are

$$\chi : \psi : w = 6.1214 : 8.3284 : 4.1825.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Two sections ground parallel to the symmetry plane $b\{010\}$ afforded identical extinction angles in the stauroscope, namely, $3^\circ 25'$, with respect to the normal to $c\{001\}$, the direction being backwards, as represented in Fig. 13. This

FIG. 13.



axis of the optical ellipsoid is, as usual in the series, the second median line, and the other at right angles in the symmetry plane is the first median line.

The *sign of double refraction* is positive, determined as before. The morphological axial angle ac being $73^\circ 57'$, the orientations are as under.

The first median line t lies in the obtuse angle of the morphological axes ac , and is inclined $3^\circ 25'$ to the axis a .

The second median line a lies also in the obtuse angle ac , and is inclined $12^\circ 38'$ to the vertical axis c .

The first median line is also inclined $86^\circ 35'$ to the normal to $c\{001\}$, and $12^\circ 38'$ to the normal to $a\{100\}$. Perrot gives $85^\circ 45'$ for the former value.

Optic Axial Angle.—Six section-plates were ground, three perpendicular to the first, and three to the second median line. The angle in air is very large and difficult to observe properly, but the

following trustworthy measurements were obtained for the three brighter colours.

Determination of apparent Angle in Air of Rubidium Nickelous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
C	155° 55'	156° 15'	156° 0'	156° 3'
Na	156 45	157 25	156 50	157 0
Tl	157 30	158 40	158 5	158 5

Determination of true Optic Axial Angle of Rubidium Nickelous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li	{ 1 2 3	{ 72° 55' 73 12 72 56	{ 1a 2a 3a	{ 86° 12' 86 0 86 32	{ 82° 2' 82 20 81 52	{ 82° 5'
C	{ 1 2 3	{ 72 52 73 3 72 48	{ 1a 2a 3a	{ 86 9 85 51 86 22	{ 82 2 82 18 81 52	{ 82 4
Na	{ 1 2 3	{ 72 32 72 37 72 28	{ 1a 2a 3a	{ 85 47 85 34 85 58	{ 82 0 82 10 81 50	{ 82 0
Tl	{ 1 2 3	{ 72 7 72 5 72 8	{ 1a 2a 3a	{ 85 22 85 5 85 36	{ 81 56 82 4 81 48	{ 81 56
F	{ 1 2 3	{ 71 38 71 30 71 34	{ 1a 2a 3a	{ 85 3 84 35 85 6	{ 81 46 81 56 81 42	{ 81 48

The immersion liquid for 2Ha and 2Ho was in every case monobromonaphthalene. The order of dispersion was confirmed by observation with white light in toluene, whose refractive index is near the mean index of the crystal. One brush was practically devoid of colour, while the other was brightly fringed with red inside (nearest the first median line), and blue outside, indicating a larger angle for red than for blue.

Perrot gives 81° 43' as the true angle for yellow light.

Dispersion of the Median Lines.—The optic axis which remains nearly constant for all wave-lengths is the one which emerges nearly normal to $r\{201\}$, the other, which is furthest removed from the stationary axis for red, is that emerging about 10° from $r'\{201\}$. Hence the first median line is dispersed in such order that it lies nearer the morphological axis a for red than it does for blue, the amount of dispersion being about 10'.

Effect of Rise of Temperature on the Optic Axial Angle.—Section 2 was heated to 70°, when the apparent angle in air was found to be 158° 55'. Hence 2E increases $1\frac{1}{2}^\circ$ for 50° rise of temperature.

Refractive Indices.—Six prisms were employed, ground upon three crystals, a complementary pair upon each. The results are as follows.

Determination of Refractive Indices of Rubidium Nickelous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Mean refractive index.	Perrot's values.
α Vibrations parallel 2nd median line α .	Li	1.4870	1.4869	1.4864	1.4868	—
	C	1.4874	1.4872	1.4871	1.4872	1.4874
	Na	1.4894	1.4897	1.4894	1.4895	1.4896
	Tl	1.4922	1.4922	1.4917	1.4920	—
	F	1.4950	1.4951	1.4947	1.4949	1.4951
	G	1.4999	1.4995	1.4993	1.4996	—
β Vibrations parallel symmetry axis b .	Li	1.4935	1.4933	1.4932	1.4933	—
	C	1.4939	1.4937	1.4936	1.4937	1.4943
	Na	1.4962	1.4961	1.4961	1.4961	1.4967
	Tl	1.4989	1.4986	1.4986	1.4987	—
	F	1.5020	1.5017	1.5015	1.5017	1.5022
	G	1.5063	1.5062	1.5060	1.5062	—
γ Vibrations parallel 1st median line c .	Li	1.5023	1.5023	1.5022	1.5023	—
	C	1.5027	1.5027	1.5026	1.5027	1.5033
	Na	1.5054	1.5051	1.5051	1.5052	1.5058
	Tl	1.5080	1.5079	1.5075	1.5078	—
	F	1.5112	1.5111	1.5108	1.5110	1.5118
	G	1.5157	1.5154	1.5158	1.5156	—

The intermediate axis β , corrected to a vacuum, is accurately expressed, for any wave length λ , by the following formula.

$$\beta = 1.4838 + \frac{454\,708}{\lambda^2} - \frac{486\,600\,000\,000}{\lambda^4} + \dots$$

The α indices are given by the formula very closely if the constant 1.4838 is diminished by 0.0066 and the γ values if it is increased by 0.0091. The former being the lesser difference determines the sign of double refraction to be positive.

Effect of Rise of Temperature on Refraction.—Determinations of refractive index at 70° indicate that the indices are lowered about 0.0015 for 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices just given lead to the following values of these ratios

$$a : b : c = 1.0044 : 1 : 0.9940.$$

Molecular Optical Constants.—The indices when combined with the density and molecular weight yield the following numbers for these constants.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \cdot$	$\left\{ \begin{array}{l} \text{C. } 0.1115 \\ \text{G. } 0.1139 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1127 \\ 0.1151 \end{array} \right.$	$\left\{ \begin{array}{l} 0.1145 \\ 0.1169 \end{array} \right.$
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	$\left\{ \begin{array}{l} \text{C. } 59.00 \\ \text{G. } 60.27 \end{array} \right.$	$\left\{ \begin{array}{l} 59.67 \\ 60.94 \end{array} \right.$	$\left\{ \begin{array}{l} 60.59 \\ 61.90 \end{array} \right.$
Specific dispersion, $n_G - n_C$	0.0024	0.0024	0.0024
Molecular dispersion, $m_G - m_C$	1.27	1.27	1.31
Molecular refraction $\frac{n^2 - 1}{d} M$	C. 99.92	101.25	103.09

These values are independent of temperature, as density and refraction vary in the same direction on change of temperature.

Cæsium Nickelous Sulphate, $\text{Cs}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

A well-defined *cleavage* parallel $r'\{201\}$ is exhibited by the crystals of this salt in common with the rest of the series. Its direction was proved to be precisely 180° from r' by measurement on the goniometer, the cleaved surfaces reflecting sharp images of the signal.

Volume.

Relative Density.—Four determinations were made with different crops derived from two independent preparations. The results are as under.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3.5401	2.8645
3.1240	2.8701
4.1118	2.8617
4.9850	2.8649

Mean 2.8653

$$\text{Molecular Volume. } \frac{M}{d} = \frac{624.3}{2.865} = 217.91.$$

Distance Ratios.—The axial ratio was previously shown to be

$$a : b : c = 0.7270 : 1 : 0.4984,$$

and the axial angle $\beta 72^\circ 58'$. Combining these with the molecular volume, we obtain the following distance ratios.

$$\chi : \psi : \omega = 6.2289 : 8.5680 : 4.2703.$$

Optics.

The crystals of cæsium nickelous sulphate exhibit optical properties of a particularly interesting nature. The sign of double refraction is negative, the reverse of what usually obtains in the series, and this is accompanied by a reversal of the median lines. Moreover, this

Optic Axial Angle.—Three pairs of section-plates were ground perpendicular to the two directions of extinction in the symmetry plane, and it was on measuring the apparent optic axial angle in monobromonaphthalene exhibited by the first pair of sections, that it was found that the angle afforded by the plate perpendicular to what is generally the first median line in the series, was larger than the angle indicated by the section ground in the direction at right angles to this, and that therefore the median lines are reversed. Both angles are very large, so much so that none of the sections exhibited the optic axial brushes in air, only portions of rings. The following are the measurements with the various sections in monobromonaphthalene.

Determination of true Optic Axial Angle of Cæsium Nickelous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean value of 2Va.
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 78^{\circ} 20' \\ 78 16 \\ 78 24 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 82^{\circ} 51' \\ 83 0 \\ 83 5 \end{array} \right.$	$\left\{ \begin{array}{l} 87^{\circ} 20' \\ 87 12 \\ 87 14 \end{array} \right.$	$87^{\circ} 15'$
C.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 78 15 \\ 78 12 \\ 78 18 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 82 45 \\ 82 54 \\ 82 57 \end{array} \right.$	$\left\{ \begin{array}{l} 87 21 \\ 87 14 \\ 87 16 \end{array} \right.$	$87 17$
Na	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 78 2 \\ 77 59 \\ 78 1 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 82 28 \\ 82 24 \\ 82 30 \end{array} \right.$	$\left\{ \begin{array}{l} 87 22 \\ 87 22 \\ 87 20 \end{array} \right.$	$87 21$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 77 42 \\ 77 44 \\ 77 42 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 81 54 \\ 81 53 \\ 82 1 \end{array} \right.$	$\left\{ \begin{array}{l} 87 29 \\ 87 31 \\ 87 26 \end{array} \right.$	$87 29$
F.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 77 23 \\ 77 15 \\ 77 18 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 81 10 \\ 81 10 \\ 81 13 \end{array} \right.$	$\left\{ \begin{array}{l} 87 43 \\ 87 38 \\ 87 38 \end{array} \right.$	$87 40$

The order of dispersion was confirmed by observation of the interference figures afforded by Sections 1, 2, and 3 in cedar oil, whose refractive index is very nearly the same as the mean index of the crystal. Both the order of the colours in white light, and actual measurements for C and Tl light, indicate a larger angle for blue than for red light. One of the axial brushes was practically immovable for all changes of wave-length, whilst the other axis was considerably dispersed, being farthest from the immovable axis for blue light.

Dispersion of the Median Lines.—The observations in cedar oil were supplemented by similar ones in benzene, whose refractive index is only slightly different from the mean index of the crystal but on the other side of that mean to cedar oil. Hence the mean of the two series of observations will probably be very near the truth. In cedar oil, the immovable axis was the one which emerges between $a\{100\}$

and $r\{201\}$, the axis which showed considerable dispersion being approximately normal to $s'\{\bar{1}01\}$ (*vide* spherical projection, previous memoir, 403).³⁴³ In benzene, both axes showed dispersion, but only a very small amount, apparently the axis normal to $s'\{\bar{1}01\}$ least. In both cases, the first median line was nearer to the vertical axis c for blue than for red. The true dispersion of the axes themselves would appear to be that the axis emerging between $a\{100\}$ and $r\{201\}$ is very slightly dispersed and the other normal to $s'\{\bar{1}01\}$ more so, the order for the two ends of the spectrum being as follows.

red blue	1st median line	red blue
axis between	for for	axis normal
$a\{100\}$ and $r\{201\}$.	red. blue.	to $s'\{\bar{1}01\}$.

From the readings in monochromatic light, the first median line would appear to be nearer the vertical morphological axis c by about 15' for F than it is for Li light.

The effect of rise of temperature could not be determined as the optic axes did not emerge in air owing to their large internal angle.

Refractive Indices.—These were determined with six prisms, ground upon three different crystals, a pair upon each. The results are given in the accompanying table.

Determination of Refractive Indices of Caesium Nickelous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Mean refrac- tive index.
α Vibrations par- allel 1st median line a . ($7^\circ 3'$ from normal to $c\{001\}$).	Li	1.5067	1.5060	1.5056	1.5061
	C	1.5070	1.5064	1.5060	1.5065
	Na	1.5093	1.5086	1.5082	1.5087
	Tl	1.5118	1.5110	1.5109	1.5112
	F	1.5150	1.5145	1.5143	1.5146
	G	1.5198	1.5190	1.5189	1.5192
β Vibrations parallel symmetry axis b (b).	Li	1.5103	1.5097	1.5101	1.5100
	C	1.5106	1.5101	1.5105	1.5104
	Na	1.5130	1.5125	1.5131	1.5129
	Tl	1.5156	1.5151	1.5156	1.5154
	F	1.5189	1.5185	1.5187	1.5187
	G	1.5229	1.5238	1.5238	1.5235
γ Vibrations parallel 2nd median line r .	Li	1.5134	1.5130	1.5135	1.5133
	C	1.5138	1.5134	1.5139	1.5137
	Na	1.5164	1.5161	1.5162	1.5162
	Tl	1.5189	1.5189	1.5189	1.5189
	F	1.5221	1.5221	1.5221	1.5221
	G	1.5263	1.5261	1.5273	1.5266

It will be observed that the directions of vibration for the three

indices are as usual in the series, the direction for α , however, usually the second median line, is, in this salt, the first median line, and for γ the second median line instead of the first median line as usual.

The intermediate index β , corrected to a vacuum, is accurately expressed, for any wave-length λ to near F, by the formula

$$\beta = 1.4980 + \frac{634\ 374}{\lambda^2} - \frac{3\ 582\ 100\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced if the constant 1.4980 is diminished by 0.0041, and the γ values if it is increased by 0.0033. The former difference being greater than the latter, instead of less as usual throughout the series, determines the sign of double refraction to be negative.

Effect of Rise of Temperature on Refraction.—Determinations at 70° indicate that the indices are lowered about 0.0016 by 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices of refraction furnish the following ratios along the three rectangular directions of vibration.

$$a : b : c = 1.0028 : 1 : 0.9978.$$

Molecular Optical Constants.—The calculated values of these constants are as under.

Axis of optical ellipsoid.....	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1039 G. 0.1061	0.1045 0.1068	0.1051 0.1073
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$			
Specific dispersion, $n_G - n_C \dots$	0.0022	0.0023	0.0022
Molecular dispersion, $m_G - m_C \dots$	1.36	1.40	1.38
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 110.46	111.31	112.03

These values will, as in the cases of the previous salts, be for the same reason independent of temperature.

SALTS CONTAINING COBALT.

Potassium Cobaltous Sulphate, $K_2Co(SO_4)_2 \cdot 6H_2O$.

Cleavage occurs readily parallel $r'\{\bar{2}01\}$; the position of the cleaved surfaces was goniometrically verified to be 180° from the r' faces, the images of the signal being sharply defined.

Volume.

Relative Density.—Four determinations with good crystals yielded the following results.

The second median line a lies also in the obtuse axial angle ac , and is inclined $10^{\circ} 5'$ to the vertical axis c .

The first median line is also inclined $85^{\circ} 10'$ to the normal to $c\{001\}$ and $10^{\circ} 5'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Six section-plates were ground, three perpendicular to the first, and three to the second median line. Owing to the large amount of absorption at the blue end of the spectrum by the deep brownish-red crystals of this salt, measurements of the apparent optic axial angle in air and in monobromonaphthalene for F light are more difficult to obtain than usual, and require a powerful source of light; it was consequently necessary to open the receiving slit of the monochromatic illuminator more than usual for the observations with F light.

Determination of the apparent Angle in Air of Potassium Cobaltous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$114^{\circ} 50'$	$113^{\circ} 12'$	$113^{\circ} 46'$	$113^{\circ} 56'$
C	114 54	113 16	113 51	114 0
Na	115 26	113 40	114 8	114 25
Tl	116 7	114 12	114 28	114 56
F	117 0	115 0	115 0	115 40

Murmann and Rotter give $110^{\circ} 10'$ as the apparent angle in air; they further state that both axes are nearer to the median line for red than for blue, hence the angle was larger for blue, which agrees with the above measurements.

Determination of true Optic Axial Angle of Potassium Cobaltous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of $2Ha$.	No. of section perp. 2nd median line.	Observed values of $2Ho$.	Calculated values of $2Va$.	Mean $2Va$.
Li	{ 1	$61^{\circ} 32'$	$1a$	$96^{\circ} 1'$	$69^{\circ} 5'$	$68^{\circ} 38'$
	{ 2	60 48	$2a$	96 16	68 24	
	{ 3	60 52	$3a$	96 21	68 25	
C	{ 1	61 30	$1a$	95 48	69 8	68 39
	{ 2	60 46	$2a$	96 11	68 24	
	{ 3	60 49	$3a$	96 15	68 25	
Na	{ 1	61 21	$1a$	95 23	69 12	68 41
	{ 2	60 34	$2a$	95 45	68 26	
	{ 3	60 37	$3a$	95 51	68 26	
Tl	{ 1	61 14	$1a$	94 55	69 18	68 44
	{ 2	60 21	$2a$	95 15	68 28	
	{ 3	60 25	$3a$	95 23	68 28	
F	{ 1	61 0	$1a$	94 20	69 22	68 48
	{ 2	60 3	$2a$	94 35	68 31	
	{ 3	60 10	$3a$	94 50	68 30	

The immersion liquid employed was monobromonaphthalene. Different crops of this salt appear to exhibit somewhat greater differences of optic axial angle than usual. The crystals investigated were from the same preparation as that used for the morphological work, and shown by analysis to be pure.

Murmann and Rotter give the true angle as $66^{\circ} 56'$, but only one plate was employed, and the true angle calculated by use of the mean refractive index of the salt, and the index of the immersion oil employed. They further state that the true optic axial angle is less for red than for blue.

The order of dispersion was confirmed with Sections 1 and 3 by measurements while immersed in toluene, whose refractive index is almost exactly the mean of the crystal indices. The amount of dispersion indicated was very small, which agrees with the calculated amount shown in the table of results, but the angle for blue was decidedly larger than that for red.

Dispersion of the Median Lines.—The observations in toluene indicated clearly that the first median line is dispersed so that for red it lies nearer to the morphological axis a than for blue. This agrees with the observation of Murmann and Rotter. The amount indicated was $10-15'$. Both axes exhibited slight dispersion in the same direction, the one near the normal to $r'\{201\}$ least.

Effect of Rise of Temperature on the Optic Axial Angle.—Measurement of the apparent angle in air with Section 1 at 70° indicated that $2E$ increases about $2^{\circ} 15'$ for 50° rise of temperature.

Refractive Indices.—The six prisms employed were ground upon five different crystals, and the results are given in the accompanying table. The readings for F light were quite trustworthy, the absorption in the crystal not being very material.

As was observed with respect to the optic axial angle, different crops exhibit slight differences of refractive index.

Murmann and Rotter ascribe the values to β for red 1.482 , for yellow 1.487 , and for green 1.490 . *See notes, V. 692, p. 1756*

The intermediate α and β , corrected to a vacuum, is expressed, for any wave-length as far as F, by the formula

$$\beta = 1.4737 + \frac{514\ 824}{\lambda^2} - \frac{1\ 962\ 700\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced if the constant 1.4737 is diminished by 0.0058 , and the γ values if it is increased by 0.0138 . The former difference being the smaller, determines that the sign of double refraction is, as previously stated, positive.

Determination of Refractive Indices of Potassium Cobaltous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 1 prism.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Crystal 5, 1 prism.	Mean refractive index.
α Vib. par. 2nd median line α .	Li	1·4771	1·4789	1·4781	—	—	1·4780
	C	1·4775	1·4793	1·4785	—	—	1·4784
	Na	1·4795	1·4817	1·4808	—	—	1·4807
	Tl	1·4819	1·4839	1·4831	—	—	1·4830
	F	1·4850	1·4871	1·4861	—	—	1·4861
	G	1·4892	1·4916	—	—	—	1·4904
β Vib. par. symmetry axis b (h)	Li	1·4832	1·4849	1·4842	1·4836	1·4829	1·4838
	C	1·4836	1·4853	1·4846	1·4840	1·4833	1·4842
	Na	1·4860	1·4877	1·4869	1·4866	1·4853	1·4865
	Tl	1·4884	1·4900	1·4895	1·4889	1·4875	1·4889
	F	1·4915	1·4932	1·4924	1·4919	1·4905	1·4919
	G	1·4958	1·4972	—	1·4964	1·4949	1·4961
γ Vib. par. 1st median line ϵ .	Li	1·4975	—	—	1·4973	1·4971	1·4973
	C	1·4980	—	—	1·4977	1·4975	1·4977
	Na	1·5006	—	—	1·5004	1·5001	1·5004
	Tl	1·5032	—	—	1·5028	1·5023	1·5028
	F	1·5065	—	—	1·5058	1·5055	1·5059
	G	1·5106	—	—	1·5111	1·5097	1·5105

Effect of Rise of Temperature on Refraction.—Determinations of refractive index at 70° indicated a lowering of the indices by about 0·0020 for 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The values of these constants, derived from the indices, are as under.

$$a : b : c = 1·0039 : 1 : 0·9907.$$

Molecular Optical Constants.—The following values were deduced from the indices, combined with the density and molecular weight.

Axis of optical ellipsoid	α .	b .	c .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n..$	{ C. 0·1282 G. 0·1309	0·1295 0·1322	0·1325 0·1354
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m..$			
Specific dispersion, $n_G - n_C$	C. 56·08	56·66	58·00
	G. 57·28	57·84	59·26
Specific dispersion, $n_G - n_C$	0·0027	0·0027	0·0029
Molecular dispersion, $m_G - m_C$	1·20	1·18	1·26
Molecular refraction, $\frac{n^2 - 1}{d} M$	C. 94·72	95·87	98·54

These values will be substantially constant for all temperatures at which the crystals of the salt are capable of existing, as refraction and density vary in the same direction for change of temperature.

Rubidium Cobaltous Sulphate, $\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

The crystals exhibited an excellent *cleavage* parallel $r'\{201\}$. The direction was proved to be exactly 180° from r' by goniometrical measurement, the fractures affording well-defined images of the signal.

Volume.

Relative Density.—Four determinations were made with different crops of clear crystals derived from two independent preparations; the two last determinations were carried out with crystals which were respectively dark brownish-red and ruby-red, in order to ascertain if any difference in density were apparent. The results will be seen, from the table given below, to be nearly identical in these two cases.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3.7399	2.5529
4.8409	2.5571
5.9019	2.5573
4.9051	2.5591

Mean 2.5566

Perrot ascribes the density 2.56 to this salt, his individual values varying from 2.540 to 2.577.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{530}{2.557} = 207.28.$$

Distance Ratios.—The axial angle was previously shown to be $73^\circ 59'$, and the ratio of the axes

$$a : b : c = 0.7391 : 1 : 0.5011.$$

Upon combination of these constants with the molecular volume, the following distance ratios are obtained.

$$\chi : \psi : w = 6.1718 : 8.3505 : 4.1844.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Two section-plates ground parallel to the symmetry plane $b\{010\}$ exhibited the following extinction angles with respect to the normal to $c\{001\}$.

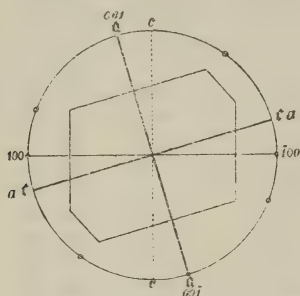
Section 1.....	$0^\circ 10'$ forwards.
Section 2.....	0 10 backwards.

Mean 0 0

The direction of extinction is thus found to be exactly normal to the basal plane, as represented in Fig. 16. This direction is the

second median line, the first median line being coincident with the crystallographical axis a .

FIG. 16.



The *sign of double refraction* is positive, proved as in the cases of the foregoing salts. The morphological axial angle being $73^{\circ} 59'$, the orientation is as follows.

The first median line ϵ is coincident with the morphological axis a . The second median line a lies in the obtuse angle of the morphological axes ac ; it is precisely normal to $c\{001\}$, and is inclined $16^{\circ} 1'$ to the vertical axis c .

The first median line is consequently inclined exactly 90° to the normal to $c\{001\}$, and is inclined $16^{\circ} 1'$ to the normal to $a\{100\}$.

Perrot states that the first median line is inclined $85^{\circ} 15'$ to the normal to $\{001\}$, which differs somewhat from the orientation of the principal optical directions afforded by the author's crystals.

Optic Axial Angle.—Three section-plates were ground perpendicular to the first median line. The fact that the second median line is exactly normal to the basal plane rendered it unnecessary to grind plates perpendicular to this median line, and three crystals exhibiting plane and large $c\{001\}$ faces were consequently employed for the observations of $2H_o$. Powerful illumination is required with F light, owing to absorption by the red crystals.

Determination of apparent Angle in Air of Rubidium Cobaltous Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$129^{\circ} 28'$	$129^{\circ} 24'$	$130^{\circ} 25'$	$129^{\circ} 46'$
C.....	129 34	129 28	130 30	129 51
Na	129 54	129 48	130 51	130 10
Tl.....	130 9	130 6	131 12	130 29
F.....	130 35	130 33	131 38	130 55

Determination of true Optic Axial Angle of Rubidium Cobaltous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of plate perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66^{\circ} 18' \\ 66 \quad 38 \\ 66 \quad 56 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 90^{\circ} 12' \\ 91 \quad 4 \\ 91 \quad 22 \end{array} \right.$	$\left\{ \begin{array}{l} 75^{\circ} 20' \\ 75 \quad 10 \\ 75 \quad 15 \end{array} \right.$	$\left. \right\} 75^{\circ} 15'$
C.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \quad 15 \\ 66 \quad 33 \\ 66 \quad 53 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 90 \quad 9 \\ 90 \quad 59 \\ 91 \quad 18 \end{array} \right.$	$\left\{ \begin{array}{l} 75 \quad 19 \\ 75 \quad 8 \\ 75 \quad 14 \end{array} \right.$	$\left. \right\} 75 \quad 14$
Na....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 66 \quad 0 \\ 66 \quad 18 \\ 66 \quad 39 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 89 \quad 52 \\ 90 \quad 46 \\ 91 \quad 0 \end{array} \right.$	$\left\{ \begin{array}{l} 75 \quad 16 \\ 75 \quad 4 \\ 75 \quad 12 \end{array} \right.$	$\left. \right\} 75 \quad 11$
Tl....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 40 \\ 66 \quad 0 \\ 66 \quad 24 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 89 \quad 30 \\ 90 \quad 26 \\ 90 \quad 40 \end{array} \right.$	$\left\{ \begin{array}{l} 75 \quad 12 \\ 75 \quad 0 \\ 75 \quad 11 \end{array} \right.$	$\left. \right\} 75 \quad 8$
F.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \quad 12 \\ 65 \quad 36 \\ 66 \quad 2 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 89 \quad 0 \\ 90 \quad 0 \\ 90 \quad 12 \end{array} \right.$	$\left\{ \begin{array}{l} 75 \quad 6 \\ 74 \quad 54 \\ 75 \quad 8 \end{array} \right.$	$\left. \right\} 75 \quad 3$

The immersion liquid was monobromonaphthalene in each case for the observation of 2Ha and 2Ho. The order of dispersion was confirmed by observations in toluene, whose index of refraction is the same as the β index of the crystals; the angle for red was clearly larger than that for blue.

Perrot gives the angle as $75^{\circ} 5'$ for sodium light.

Dispersion of the Median Lines.—The observations in toluene clearly indicated that the optic axis which emerges between $a\{100\}$ and $r\{201\}$ is invariable for all colours, whilst the other axis is dispersed so that for red it is furthest removed from the immovable axis. The first median line is consequently dispersed so that for blue it is $8-10'$ nearer to the immovable axis than for red.

Effect of Rise of Temperature on the Optic Axial Angle.—Measurements with Section 1 at 70° indicate that the apparent optic axial angle in air increases about 2° for 50° rise of temperature.

Refractive Indices.—Six prisms were ground upon four different crystals; the results obtained with them are given in the accompanying table. The absorption for F light was insufficient to cause material trouble in obtaining good readings for this wave-length.

As in the case of the potassium cobalt salt, different crops are found to exhibit slight differences of refractive index. Perrot remarked this, and convinced himself that they were not due to impurity, a conclusion which is fully borne out by the present work with preparations of undoubted purity.

The intermediate index β , corrected for a vacuum, is accurately expressed, for any wave-length λ as far as F, by the formula

$$\beta = 1.4789 + \frac{507\ 763}{\lambda^2} - \frac{1\ 841\ 600\ 000\ 000}{\lambda^4} + \dots$$

The α indices are very closely reproduced if the constant 1.4789 is diminished by 0.0057, and the γ indices if it is increased by 0.0098. The positive nature of the double refraction is evident from the fact that the former is the smaller difference from β .

Determination of Refractive Indices of Rubidium Cobaltous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.	Perrot's values.
α Vibs. par. 2nd median line	Li	1.4825	1.4840	—	1.4834	1.4833	—
	C	1.4829	1.4844	—	1.4838	1.4837	1.4834
	Na	1.4852	1.4864	—	1.4861	1.4859	1.4860
	Tl	1.4875	1.4889	—	1.4882	1.4882	—
	F	1.4904	1.4916	—	1.4910	1.4910	1.4912
	G	1.4948	1.4960	—	—	1.4954	—
β Vibs. par. symmetry axis <i>b</i> (<i>h</i>)	Li	1.4878	1.4891	1.4893	1.4893	1.4889	—
	C	1.4882	1.4895	1.4896	1.4897	1.4893	1.4890
	Na	1.4904	1.4919	1.4919	1.4920	1.4916	1.4916
	Tl	1.4930	1.4943	1.4943	1.4942	1.4940	—
	F	1.4960	1.4972	1.4969	1.4970	1.4968	1.4970
	G	1.5001	1.5015	1.5018	—	1.5011	—
γ Vibs. par. 1st median line	Li	1.4976	1.4988	1.4990	—	1.4985	—
	C	1.4983	1.4991	1.4995	—	1.4989	1.4985
	Na	1.5005	1.5018	1.5018	—	1.5014	1.5012
	Tl	1.5033	1.5040	1.5041	—	1.5038	—
	F	1.5062	1.5073	1.5070	—	1.5068	1.5069
	G	1.5104	1.5119	1.5119	—	1.5114	—

Effect of Rise of Temperature on Refraction.—Determinations at 70° indicate that the indices are lowered about 0.0016 by 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—These are as follows.

$$a : b : c = 1.0038 : 1 : 0.9935.$$

Molecular Optical Constants.—The calculated values of these constants, obtained by combining the refractive indices with the molecular weight and the density, are as under.

Axis of optical ellipsoid	α .	b .	c .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1119	0.1130	0.1149
	{ G. 0.1142	0.1153	0.1173
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C. 59.31	59.90	60.89
	{ G. 60.53	61.12	62.18
Specific dispersion, $n_G - n_C \dots$	0.0023	0.0023	0.0024
Molecular dispersion, $m_G - m_C \dots$	1.22	1.22	1.29
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 100.34	101.50	103.49

These values will again be independent of temperature, as change of the latter causes both refraction and density to vary in the same direction.

Cæsium Cobaltous Sulphate, $\text{Cs}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

There is a good *cleavage* parallel $r'\{201\}$. The cleaved surfaces were proved by direct measurement to be exactly 180° from r' ; this was rendered possible by the perfection of the reflection of the goniometer signal from the plane fracture.

Volume.

Relative Density.—Four determinations were made with different crops of perfectly transparent crystals derived from two independent preparations. The results are given beneath.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.6173	2.8391
4.1226	2.8372
3.7098	2.8365
4.4523	2.8350
Mean.....	2.8370

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{625}{2.837} = 220.30.$$

Distance Ratios.—It was previously shown that the axial angle β is $72^\circ 52'$, and the axial ratio

$$a : b : c = 0.7270 : 1 : 0.4968.$$

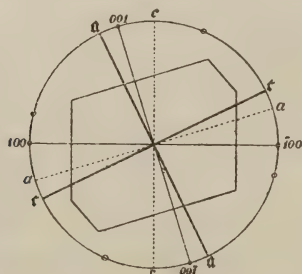
When combined with the molecular volume the following distance ratios are afforded.

$$\chi : \psi : \omega = 6.2595 : 8.6101 : 4.2775.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Two sections were ground parallel to the symmetry plane $b\{010\}$. Each exhibited an extinc-

FIG. 17.



tion angle with respect to the normal to the basal plane $c\{001\}$ of $9^\circ 0'$ forwards, as represented in Fig. 17.

This direction is the second median line, as is normally the case throughout the series, the first median line being the other direction of extinction, at 90° to this, in the symmetry plane.

The *sign of double refraction* is positive, proved as before by the quarter undulation mica and the relations of the refractive indices. The morphological axial angle ac being $72^\circ 52'$, the orientation is as follows.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $9^\circ 0'$ to the axis a .

The second median line a lies in the obtuse axial angle ac , and is inclined $26^\circ 8'$ to the vertical axis c .

The first median line is also inclined $99^\circ 0'$ to the normal to $c\{001\}$, and $26^\circ 8'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Six section-plates were ground, three perpendicular to the first and three to the second median line. The apparent angle in air is very large, and consequently difficult to observe, particularly in the case of such feebly doubly refractive substances as the cæsium salts of this series, whose section-plates require to be relatively very thick to yield well-defined interference figures. The three sections perpendicular to the first median line were very good ones, but 2E was only afforded approximately. For sodium light the values obtained were $157^\circ 50'$, $154^\circ 10'$, and $158^\circ 0'$. The mean angle $156^\circ 40'$ for 2E is probably as near the truth as can be obtained for so large an angle.

Determination of true Optic Axial Angle of Cæsium Cobaltous Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 73^\circ 45' \\ 72 \quad 35 \\ 74 \quad 8 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 87^\circ 52' \\ 86 \quad 55 \\ 87 \quad 55 \end{array} \right.$	$\left\{ \begin{array}{l} 81^\circ 43' \\ 81 \quad 26 \\ 81 \quad 56 \end{array} \right.$	$81^\circ 42'$
C.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \quad 40 \\ 72 \quad 30 \\ 74 \quad 3 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 87 \quad 47 \\ 86 \quad 52 \\ 87 \quad 52 \end{array} \right.$	$\left\{ \begin{array}{l} 81 \quad 42 \\ 81 \quad 24 \\ 81 \quad 54 \end{array} \right.$	$81 \quad 40$
Na.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \quad 25 \\ 72 \quad 5 \\ 73 \quad 50 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 87 \quad 35 \\ 86 \quad 40 \\ 87 \quad 42 \end{array} \right.$	$\left\{ \begin{array}{l} 81 \quad 38 \\ 81 \quad 13 \\ 81 \quad 51 \end{array} \right.$	$81 \quad 34$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 73 \quad 10 \\ 71 \quad 40 \\ 73 \quad 35 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 87 \quad 25 \\ 86 \quad 23 \\ 87 \quad 30 \end{array} \right.$	$\left\{ \begin{array}{l} 81 \quad 34 \\ 81 \quad 5 \\ 81 \quad 48 \end{array} \right.$	$81 \quad 29$
F.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 72 \quad 50 \\ 71 \quad 10 \\ 73 \quad 16 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 87 \quad 10 \\ 86 \quad 3 \\ 87 \quad 14 \end{array} \right.$	$\left\{ \begin{array}{l} 81 \quad 28 \\ 80 \quad 55 \\ 81 \quad 43 \end{array} \right.$	$81 \quad 22$

The true angle was determined as usual by immersion in monobromonaphthalene and observation of $2H\alpha$ and $2H\delta$. Very intense light is essential in order to measure the angles for F light.

The order of dispersion was proved by measurements with Sections 1, 2, and 3 while immersed in cedar oil, whose index of refraction is near the mean index of the crystal; the angle in each case was about $20'$ larger for red than for greenish-blue.

Dispersion of the Median Lines.—The observations in cedar oil further indicated that the optic axis which emerges between $a\{100\}$ and $r\{201\}$ is immovable for all colours, while the other axis is dispersed so that for red it is furthest from the fixed axis. The first median line is therefore dispersed so that for F light it lies about $10'$ nearer to the morphological axis a than it does for Li light.

No observations of the optic axial angle were made at higher temperatures, owing to the difficulty of obtaining exact measurements of $2E$ on account of the exceptionally large angle. The error of the measurements was about as great as the usual alteration of the angle for 50° rise of temperature.

Refractive Indices.—Six prisms were ground upon four different crystals. The results are given in the accompanying table.

Determination of Refractive Indices of Cæsium Cobaltous Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 2 prisms.	Crystal 3, 1 prism.	Crystal 4, 1 prism.	Mean refractive index.
α Vibrations parallel 2nd median line α .	Li	1.5022	1.5028	—	1.5033	1.5028
	C	1.5026	1.5032	—	1.5038	1.5032
	Na	1.5055	1.5054	—	1.5062	1.5057
	Tl	1.5077	1.5078	—	1.5083	1.5079
	F	1.5109	1.5111	—	1.5117	1.5112
	G	1.5159	1.5160	—	—	1.5159
β Vibrations parallel symmetry axis β .	Li	1.5054	1.5057	1.5059	—	1.5057
	C	1.5058	1.5061	1.5033	—	1.5061
	Na	1.5082	1.5086	1.5087	—	1.5085
	Tl	1.5108	1.5111	1.5111	—	1.5110
	F	1.5140	1.5142	1.5145	—	1.5142
	G	1.5188	1.5189	1.5188	—	1.5188
γ Vibrations parallel 1st median line γ .	Li	1.5096	1.5102	1.5103	1.5109	1.5102
	C	1.5099	1.5106	1.5107	1.5113	1.5106
	Na	1.5127	1.5131	1.5131	1.5139	1.5132
	Tl	1.5152	1.5158	1.5154	1.5159	1.5156
	F	1.5185	1.5191	1.5184	1.5189	1.5187
	G	1.5237	1.5236	1.5237	—	1.5237

The amount of absorption in the greenish-blue is not sufficient to

so seriously diminish the intensity of the images of the spectrometer slit for F light as to render the readings untrustworthy, the lime-light furnishing ample light even when the slits of the monochromatic illuminator are very fine.

The intermediate index β reduced to a vacuum is accurately expressed, for any wave-length λ as far as near F, by the following formula

$$\beta = 1.4952 + \frac{532\ 337}{\lambda^2} - \frac{1\ 971\ 500\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced by the formula if the constant 1.4952 is diminished by 0.0029, and the γ indices if it is increased by 0.0046. The former number, being the smaller, determines the positive nature of the double refraction.

Effect of Rise of Temperature on Refraction.—Determinations at 70° indicated that the refractive indices are lower at that temperature by about 0.0018 than they are at the ordinary temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—These are as follows for the crystals of this salt.

$$a : b : c = 1.0019 : 1 : 0.9969.$$

Molecular Optical Constants.—The refractive indices lead to the following constants.

Axis of optical ellipsoid.....		a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$..	{ C.	0.1043	0.1048	0.1056
	{ G.	0.1065	0.1070	0.1079
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C.	65.19	65.51	66.00
	{ G.	66.57	66.89	67.41
Specific dispersion, $n_G - n_C$		0.0022	0.0022	0.0023
Molecular dispersion, $m_G - m_C$		1.38	1.38	1.41
Molecular refraction, $\frac{n - 1}{d} M$		110.95	111.58	112.57

As in the cases of the other salts of the series these constants will be independent of temperature, refraction and density varying together for change of temperature.

SALTS CONTAINING COPPER.

Potassium Copper Sulphate, $K_2Cu(SO_4)_2 \cdot 6H_2O$.

The crystals of this salt exhibit *cleavage* parallel $r'\{\bar{2}01\}$ in common with the other salts of the series. Good images of the goniometer signal were obtained from the fractures at exactly 180° from the r' faces.

It was remarked in the former memoir concerning the morphology of the series (p. 397) that the crystals of this salt were usually more

or less opaque, and that the analytical results for SO_3 were slightly low. It was pointed out that this was certainly not due to the presence of any other salt crystallising isomorphically with it, and that, therefore, it would not affect the angles of the crystals. It was suggested that it was in all probability due to a minute quantity of foreign matter mechanically included. Further work with the salt confirms this supposition. When a thin crystal or a section-plate is examined with a high power of the microscope the opacity is seen to be due to myriads of small cavities containing mother liquor. Powdering the salt and subsequent drying for an hour at the ordinary temperature on porous porcelain, of course, removes the larger ones; but the finest powder still consists of particles retaining minute cavities. Hence the slightly low analytical results. For the goniometrical investigation this property is naturally of no consequence, and, even if it were, the crystals selected for measurement were the most transparent that could be obtained. The same applies to the optical investigation, which was necessarily carried out with crystals of the highest procurable transparency. The determinations of density are more liable to be affected by it, the effect being to lower the results. The greatest care, however, was taken to render its effect as minute as possible by bestowing special trouble on the powdering and air drying, passing the dust through a sieve of the finest platinum gauze in order to weed out all coarser particles. Evidence will be subsequently given in comparing the densities of the salts of the series, that the error has in all probability been reduced to within the limits of experimental error in carrying out density determinations.

Volume.

Relative Density.—Four determinations were carried out with the precautions above specified, the crystals employed being as transparent as could be obtained, of small size, and from different preparations. The results are stated below.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.4867	2.2228
4.1229	2.2244
4.5166	2.2227
4.1518	2.2257
Mean	<hr/> 2.2239

This mean value is considerably higher than the numbers given by Joule and Playfair, 2.164, and by Schiff, 2.137, and is, undoubtedly, very near the truth. The air-drying was not sufficiently prolonged to admit any source of error due to efflorescence, it being only con-

tinued until the particles exhibited no tendency to adhere to a glass rod.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{441}{2.224} = 198.29.$$

Distance Ratios.—The axial angle β was previously shown to be $75^\circ 32'$, and the axial ratio

$$a : b : c = 0.7490 : 1 : 0.5088.$$

The distance ratios obtained by combining these with the molecular volume are

$$: \psi : w = 6.0893 : 8.1300 : 4.1366.$$

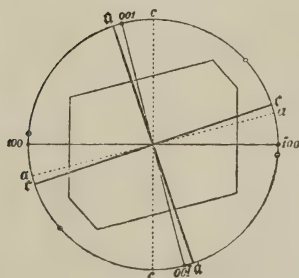
Optics.

Orientation of Axes of Optical Ellipsoid.—Two sections were ground parallel to the symmetry plane $b\{010\}$ upon two very small, but well developed and transparent, crystals. All the sections and prisms for the optical investigation of this salt were ground upon very small crystals on account of their greater transparency; there is no difficulty in carrying this out with the new grinding instrument, delicate manipulation being all that is required.

The peculiarity of the three salts containing copper, owing to the marked individuality of the latter metal as compared with that exerted by each of the dyad metals in the salts previously described, a phenomenon which was pointed out with respect to the morphology, at once begins to manifest itself in the orientation of the axes of optical elasticity. The two sections exhibited extinctions on the forward side of the normal to the basal plane, as shown in Fig. 18, whereas the potassium salts of the series usually show it behind the normal. The angles were

Section 1	4° 0'
Section 2	4 10
Mean	<hr/> 4 5

FIG. 18.



Murmann and Rotter found an extinction angle of $4^{\circ} 23'$ on the same side.

This direction is the second median line, the first median line being as usual the direction at right angles in the symmetry plane.

The sign of *double refraction* is positive. The morphological axial angle being $75^{\circ} 32'$, the following is the orientation.

The first median line, ϵ , lies in the acute angle of the morphological axes ac , and is inclined $4^{\circ} 5'$ to the axis a .

The second median line, a , lies in the obtuse angle ac , and is inclined $18^{\circ} 33'$ to the vertical axis c .

The first median line is also inclined $94^{\circ} 5'$ to the normal to $c\{001\}$, and $18^{\circ} 33'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Six sections were ground, three perpendicular to each median line, out of small, but transparent, crystals. The results obtained with them are given in the accompanying tables.

Determination of apparent Angle in Air of Potassium Copper Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$71^{\circ} 40'$	$71^{\circ} 30'$	$70^{\circ} 46'$	$71^{\circ} 19'$
C	$71 \quad 47$	$71 \quad 37$	$70 \quad 50$	$71 \quad 25$
Na	$72 \quad 42$	$72 \quad 18$	$71 \quad 20$	$72 \quad 7$
Tl	$73 \quad 43$	$73 \quad 5$	$72 \quad 20$	$73 \quad 3$
F	$75 \quad 0$	$74 \quad 0$	$73 \quad 40$	$74 \quad 13$

The apparent angle in air was given by Murmann and Rotter as $76^{\circ} 12'$.

Determination of true Optic Axial Angle of Potassium Copper Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of $2Ha$.	No. of section perp. 2nd median line.	Observed values of $2Ho$.	Calculated values of $2Va$.	Mean $2Va$.
Li	{ 1	$41^{\circ} 20'$	$1a$	$111^{\circ} 55'$	$46^{\circ} 8'$	$46^{\circ} 1'$
	{ 2	$41 \quad 13$	$2a$	$111 \quad 45$	$46 \quad 4$	
	{ 3	$41 \quad 0$	$3a$	$111 \quad 56$	$45 \quad 50$	
C	{ 1	$41 \quad 22$	$1a$	$111 \quad 50$	$46 \quad 12$	$46 \quad 6$
	{ 2	$41 \quad 17$	$2a$	$111 \quad 37$	$46 \quad 10$	
	{ 3	$41 \quad 5$	$3a$	$111 \quad 50$	$45 \quad 56$	
Na	{ 1	$41 \quad 32$	$1a$	$110 \quad 35$	$46 \quad 40$	$46 \quad 32$
	{ 2	$41 \quad 33$	$2a$	$110 \quad 45$	$46 \quad 38$	
	{ 3	$41 \quad 15$	$3a$	$110 \quad 56$	$46 \quad 18$	
Tl	{ 1	$41 \quad 45$	$1a$	$109 \quad 35$	$47 \quad 8$	$47 \quad 0$
	{ 2	$41 \quad 46$	$2a$	$109 \quad 40$	$47 \quad 7$	
	{ 3	$41 \quad 25$	$3a$	$109 \quad 50$	$46 \quad 44$	
F	{ 1	$42 \quad 0$	$1a$	$108 \quad 10$	$47 \quad 44$	$47 \quad 33$
	{ 2	$42 \quad 0$	$2a$	$108 \quad 35$	$47 \quad 38$	
	{ 3	$41 \quad 40$	$3a$	$108 \quad 35$	$47 \quad 18$	

Monobromonaphthalene was employed as immersion liquid in the measurements of $2Ha$ and $2Ho$.

An indirect determination of Murmann and Rotter by use of one plate and the mean index of refraction, afforded the angle $48^{\circ} 53'$. The dispersion is considerable, as will be seen from the table. Its order and approximate amount were confirmed by observations in toluene, whose refractive index is very near the mean index of the crystal.

Dispersion of the Median Lines.—The observations in toluene, with the two larger sections perpendicular to the first median line, indicated that the optic axis nearly normal to $r'\{201\}$ is almost fixed for all colours, whilst the other axis, not far from normal to $a\{100\}$, is dispersed, so that for blue it is furthest from the stationary axis. Hence the first median line is dispersed so that for blue it lies nearer to the crystallographic axis a than for red, the amount of difference between Li and F being a little over half a degree.

Effect of Rise of Temperature on Optic Axial Angle.—Section 1 was heated to 70° , and at this temperature the apparent angle in air 2E for C light was $80^{\circ} 30'$, for Na light $81^{\circ} 30'$, and for Tl light $82^{\circ} 30'$. Hence the apparent angle in air increases by no less than 9° for 50° rise of temperature, an amount of change larger than has been observed in any other salt of the series, excepting the abnormal cæsium magnesium salt.

Refractive Indices.—The following are the results of the determinations of refractive index, with six prisms, whose grinding upon the

Determination of Refractive Indices of Potassium Copper Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 1 prism.	Crystal 3, 2 prisms.	Crystal 4, 2 prisms.	Mean refractive index.
α Vibrations parallel 2nd median line α .	Li	—	1·4808	1·4809	1·4803	1·4807
	C	—	1·4812	1·4814	1·4807	1·4811
	Na	—	1·4836	1·4837	1·4835	1·4836
	Tl	—	1·4863	1·4862	1·4858	1·4861
	F	—	1·4895	1·4893	1·4890	1·4893
	G	—	1·4945	1·4942	—	1·4944
β Vibrations parallel symmetry axis b β .	Li	1·4834	1·4836	1·4837	1·4830	1·4834
	C	1·4838	1·4840	1·4841	1·4834	1·4838
	Na	1·4864	1·4865	1·4866	1·4859	1·4864
	Tl	1·4890	1·4891	1·4890	1·4886	1·4889
	F	1·4923	1·4924	1·4922	1·4920	1·4922
	G	—	1·4977	1·4972	—	1·4975
γ Vibrations parallel 1st median line γ .	Li	1·4993	—	1·4992	1·4985	1·4990
	C	1·4997	—	1·4996	1·4989	1·4994
	Na	1·5021	—	1·5022	1·5017	1·5020
	Tl	1·5048	—	1·5049	1·5044	1·5047
	F	1·5081	—	1·5083	1·5080	1·5081
	G	—	—	1·5134	—	1·5134

small crystals, which alone are sufficiently transparent, required unusually delicate manipulation.

The excellent agreement of the values obtained from the four different crystals affords noteworthy testimony of what can be done with the new grinding instrument. Two of the crystals employed, chosen in preference to larger ones on account of their perfect transparency and perfection of development, were scarcely larger than the head of an ordinary pin, and on one of these (crystal 3) two prisms were ground having faces which were verified to be accurately orientated in the directions theoretically desirable in order to afford all three indices. The images of the spectrometer, "Websky" slit, refracted through these miniature prisms, moreover, were quite brilliant, even up to G, using the ordinary eye-piece affording images apparently an inch long, and illuminating in the ordinary manner with the slits of the monochromatic illuminator quite fine, the lime-light being the source of light.

The rough β indices given by Murmann and Rotter differ considerably from the values now presented. They are for end red, 1.488; bright red, 1.489; yellow, 1.491; green, 1.493; greenish-blue, 1.495; and blue, 1.498.

The β indices, corrected to a vacuum, are accurately afforded, for any wave-length λ to near F, by the following formula.

$$\beta = 1.4700 + \frac{729\ 070}{\lambda^2} - \frac{5\ 063\ 700\ 000\ 000}{\lambda^4} + \dots$$

The α indices are closely reproduced (to within 0.0001) if the constant 1.4700 is diminished by 0.0028, and the γ indices if it is increased by 0.0157. The former difference, being smallest, determines that the double refraction is positive, and the relatively very small amount of that difference causes the optic axial angle also to be small.

Effect of Rise of Temperature on the Refraction.—Some difficulty was experienced in obtaining trustworthy determinations of refractive index at 70° in the case of this salt, on account of decomposition and the resulting opacity. The results indicated conclusively, however, that the indices are lowered to about the same extent as was found for the other salts of the series, the particular mean amount indicated being 0.0020, with a possible error, from the cause mentioned, of 0.0005.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices given afford the following ratios.

$$a : b : c = 1.0019 : 1 : 0.9896.$$

Molecular Optical Constants.—These are as under.

Axis of optical ellipsoid	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0·1281	0·1287	0·1322
	{ G. 0·1311	0·1318	0·1353
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C. 56·48	56·75	58·30
	{ G. 57·81	58·11	59·68
Specific dispersion, $n_G - n_C$	0·0030	0·0031	0·0031
Molecular dispersion, $m_G - m_C$	1·33	1·36	1·38
Molecular refraction, $\frac{n - 1}{d} M$	C. 95·48	96·01	99·11

These values will be independent of temperature, as alteration of the latter evokes changes of refraction and density in the same direction.

Rubidium Copper Sulphate, $Rb_2Cu(SO_4)_2 \cdot 6H_2O$.

The common *cleavage* of the series, parallel $r'\{201\}$, was verified on this salt, which exhibits it as well developed as usual. The cleaved surfaces reflected sharp images of the signal, at exactly 180° to r' .

Volume.

Relative Density.—Four determinations were made with crystals as free as possible from traces of opacity, belonging to different crops derived from two distinct preparations. The same precautions were taken as in the case of the potassium salt. The results were as stated below.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
3·4659	2·5652
3·5799	2·5682
4·9711	2·5735
4·2749	2·5726

Mean 2·5699

Perrot found the density 2·58 at 15° .

Molecular Volume.— $\frac{M}{d} = \frac{533·4}{2·570} = 207·55$.

Distance Ratios.—The axial angle was previously shown to be $74^\circ 42'$, and the axial ratio:

$$a : b : c = 0·7490 : 1 : 0·5029.$$

Combination with the molecular volume affords the following distance ratios.

$$\chi : \psi : w = 6·2147 : 8·2974 : 4·1727.$$

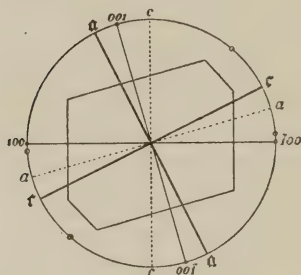
Optics.

Orientation of Axes of Optical Ellipsoid.—Two clear sections parallel to the symmetry plane $b\{010\}$ were obtained by grinding,

and found to yield the following extinction angles with respect to the normal to $c\{001\}$.

Section 1....	10° 50'
Section 2.....	11 30
Mean	<u>11 10</u>

FIG. 19.



The direction is forwards as shown in Fig. 19, and much more forwards than in any other rubidium salt of the series. This direction is, as usual in the series, the second median line, the first median line being the perpendicular direction in the symmetry plane.

The *double refraction* is of positive sign, determined by the relations of the refractive indices, and readily demonstrated by the use of the quarter undulation mica. The morphological axial angle being $74^{\circ} 42'$, the orientations are as under.

The first median line r lies in the acute angle of the morphological axes ac , and is inclined $11^{\circ} 10'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $26^{\circ} 28'$ to the vertical axis c .

The first median line is also inclined $101^{\circ} 10'$ to the normal to $c\{001\}$, and $26^{\circ} 28'$ to the normal to $a\{100\}$.

Perrot gives the inclination to $\{001\}$ as 102° .

Optic Axial Angle.—The following measurements were obtained with six section-plates, ground perpendicular to the first and second median lines.

Determination of apparent Angle in Air of Rubidium Copper Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	68° 56'	68° 30'	68° 22'	68° 36'
C	69 2	68 35	68 28	68 42
Na	69 19	69 0	69 5	69 8
Tl	69 36	69 28	69 42	69 35
F	70 0	70 10	70 25	70 12

Determination of true Optic Axial Angle of Rubidium Copper Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2H _a .	No. of section perp. 2nd median line.	Observed values of 2H _o .	Calculated values of 2V _a .	Mean 2V _a .
Li.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 39^{\circ} 49' \\ 39 44 \\ 39 51 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 113^{\circ} 5' \\ 112 50 \\ 112 40 \end{array} \right.$	$\left\{ \begin{array}{l} 44^{\circ} 24' \\ 44 23 \\ 44 32 \end{array} \right.$	$44^{\circ} 26'$
C.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 39 50 \\ 39 45 \\ 39 52 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 112 55 \\ 112 43 \\ 112 35 \end{array} \right.$	$\left\{ \begin{array}{l} 44 28 \\ 44 26 \\ 44 34 \end{array} \right.$	$44 29$
Na.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 39 53 \\ 39 49 \\ 39 55 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 112 15 \\ 112 0 \\ 111 55 \end{array} \right.$	$\left\{ \begin{array}{l} 44 40 \\ 44 40 \\ 44 46 \end{array} \right.$	$44 42$
Tl.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 39 57 \\ 39 54 \\ 39 59 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 111 30 \\ 111 17 \\ 111 10 \end{array} \right.$	$\left\{ \begin{array}{l} 44 54 \\ 44 54 \\ 45 2 \end{array} \right.$	$44 57$
F.....	$\left\{ \begin{array}{l} 1 \\ 2 \\ 3 \end{array} \right.$	$\left\{ \begin{array}{l} 40 2 \\ 40 0 \\ 40 5 \end{array} \right.$	$\left\{ \begin{array}{l} 1a \\ 2a \\ 3a \end{array} \right.$	$\left\{ \begin{array}{l} 110 40 \\ 110 20 \\ 110 20 \end{array} \right.$	$\left\{ \begin{array}{l} 45 12 \\ 45 14 \\ 45 20 \end{array} \right.$	$45 15$

Monobromonaphthalene was the immersion liquid for 2H_a and 2H_o. The order of dispersion was confirmed by observations in toluene, which clearly indicated that the angle for blue is greater than that for red.

Perrot found it $44^{\circ} 30'$ for sodium light, using a plate approximately perpendicular to the first median line, and knowing the β index of refraction.

Dispersion of the Median Lines.—The observations in toluene further indicated that the optic axis which emerges between $r'\{20\bar{1}\}$ and $s'\{10\bar{1}\}$ is almost constant for all colours, whilst the other axis nearly normal to $a\{100\}$ is dispersed so that for red it is nearer to the fixed axis than it is for blue. The first median line, therefore, is dispersed so that for blue it lies nearer to the morphological axis a than it does for red; the amount of dispersion indicated between Li and F was about $15'$.

Effect of Rise of Temperature on Optic Axial Angle.—Section 2 was heated to 70° , and the apparent angle in air measured at that temperature. It was found to be $72^{\circ} 45'$ for sodium light. Hence 2E increases about $3^{\circ} 45'$ for 50° rise of temperature.

Refractive Indices.—The indices were determined with six prisms ground upon four different crystals. The results are as given in the accompanying table (p. 440).

The β indices, corrected to a vacuum, are accurately expressed, for any wave-length λ to beyond F, by the following formula.

$$\beta = 1.4791 + \frac{392\ 159}{\lambda^2} + \frac{726\ 600\ 000\ 000}{\lambda^4} + \dots\dots\dots$$

2 H 2

Determination of Refractive Indices of Rubidium Copper Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2, 1 prism.	Crystal 3, 2 prisms.	Crystal 4, 1 prism.	Mean refrac- tive index.	Perrot's values.
α Vibs. par. 2nd me- dian line	Li	1·4858	1·4853	1·4863	1·4860	1·4858	—
	C	1·4862	1·4857	1·4867	1·4863	1·4862	1·4859
	Na	1·4886	1·4881	1·4892	1·4887	1·4886	1·4885
	Tl	1·4911	1·4906	1·4917	1·4915	1·4912	—
	F	1·4943	1·4938	1·4948	1·4944	1·4943	1·4944
	G	—	1·4988	1·4994	1·4990	1·4991	—
β Vibs. par. symmetry axis <i>b</i> (<i>b</i>)	Li	1·4878	1·4873	1·4883	—	1·4878	—
	C	1·4882	1·4877	1·4887	—	1·4882	1·4880
	Na	1·4906	1·4901	1·4912	—	1·4906	1·4906
	Tl	1·4932	1·4928	1·4938	—	1·4933	—
	F	1·4966	1·4962	1·4971	—	1·4966	1·4968
	G	1·5012	1·5010	1·5018	—	1·5013	—
γ Vibs. par. 1st me- dian line <i>c</i>	Li	1·5004	—	1·5006	1·5010	1·5007	—
	C	1·5008	—	1·5010	1·5014	1·5011	1·5008
	Na	1·5030	—	1·5037	1·5041	1·5036	1·5032
	Tl	1·5061	—	1·5064	1·5067	1·5064	—
	F	1·5095	—	1·5098	1·5102	1·5098	1·5095
	G	1·5142	—	1·5150	1·5151	1·5148	—

The α indices are very closely reproduced if the constant 1·4791 is diminished by 0·0021, and the γ indices if it is increased by 0·0130. The former difference being the smaller determines the positive nature of the double refraction; it is even relatively smaller than in the potassium salt, and hence the optic axial angle is less.

Effect of Rise of Temperature on the Refraction.—Determinations at 70° indicate that the indices are lowered about 0·0015 by 50° rise of temperature.

Ratio of Axes of Optical Velocity Ellipsoid.—The calculated values of these ratios are as under.

$$a : b : c = 1\cdot0013 : 1 : 0\cdot9914.$$

Molecular Optical Constants.—The refractive indices combined with the molecular weight and the density afford the following optical constants.

Axis of optical ellipsoid.....	α .	b .	c .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0·1118	0·1122	0·1147
	{ G. 0·1143	0·1148	0·1174
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$	{ C. 59·65	59·86	61·20
	{ G. 60·99	61·22	62·61
Specific dispersion, $n_G - n_C \dots$	0·0025	0·0026	0·0027
Molecular dispersion, $m_G - m_C \dots$	1·34	1·36	1·41
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 100·99	101·41	104·09

These constants are again practically independent of temperature, as the refraction has been shown to diminish with rise of temperature, that is, to change in the same direction as does the density when the temperature is altered.

Cæsium Copper Sulphate, $\text{Cs}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

There is an excellent *cleavage* parallel $r'\{\bar{2}01\}$, as usual in the series. Perfect reflections, at 180° from the r' faces, were obtained from the fractured surfaces.

The crystals of this salt are readily obtained quite free from turbidity, as stated in the former communication. Both the volume work and the optical investigation were carried out with very perfect specimens.

Volume.

Relative Density.—Four determinations were made with different crops belonging to two distinct preparations. The results were as given below.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.3268	2.8500
5.0172	2.8561
4.5351	2.8535
3.4604	2.8565
Mean	2.8540

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{628.4}{2.854} = 220.19.$$

Distance Ratios.—The axial angle β was previously found to be $73^\circ 50'$, and the axial ratio

$$a : b : c = 0.7429 : 1 : 0.4946.$$

The distance ratios obtained by combining these with the molecular volume are

$$\chi : \psi : w = 6.3481 : 8.5450 : 4.2263.$$

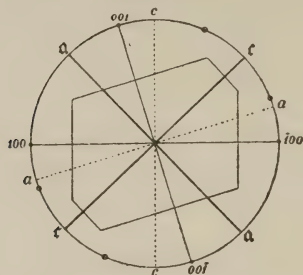
Optics.

Orientation of Axes of Optical Ellipsoid.—Two sections ground parallel to the symmetry plane $b\{010\}$, exhibited the following extinction angles with respect to the normal to the basal plane $c\{001\}$.

Section 1	$26^\circ 45'$
Section 2	26 50
*	26 47

The direction is forwards, as indicated in Fig. 20.

FIG. 20.



This is again the second median line, the first median line being at right angles to it in the symmetry plane.

The *sign of double refraction* is positive, demonstrated and proved as in the cases previously considered. The morphological axial angle being $73^{\circ} 50'$, the orientations are as follows.

The first median line ϵ lies in the acute angle of the morphological axes ac , and is inclined $26^{\circ} 47'$ to the morphological axis a .

The second median line a lies in the obtuse angle ac , and is inclined $42^{\circ} 57'$ to the vertical axis c .

The first median line is also inclined $116^{\circ} 47'$ to the normal to $c\{001\}$, and $42^{\circ} 57'$ to the normal to $a\{100\}$, and is only $27'$ removed from being exactly normal to $r'\{20\bar{1}\}$.

Optic Axial Angle.—Six excellent sections were ground, three perpendicular to the first, and three to the second, median line, and afforded the results given in the accompanying tables.

Determination of apparent Angle in Air of Cæsium Copper Sulphate.

Nature of light.	Section 1.	Section 2.	Section 3.	Mean 2E.
Li	$67^{\circ} 30'$	$67^{\circ} 25'$	$67^{\circ} 22'$	$67^{\circ} 26'$
C	67 35	67 32	67 28	67 32
Na	68 5	68 11	68 0	68 5
Tl	68 40	68 50	68 29	68 40
F	69 27	69 40	69 5	69 24

Monobromonaphthalene was used as immersion liquid in the measurement of $2H_a$ and $2H_o$. The order of dispersion was confirmed by observations in cedar oil, whose refractive index is very nearly the same as the mean index of the crystal; the angle was clearly larger for blue than for red.

Dispersion of the Median Lines.—The observations in cedar oil indicated that the optic axis emerging nearly parallel to the morphological axis a is practically immovable for all colours, whilst the other axis nearly normal to $s'\{10\bar{1}\}$ is dispersed, so that for blue it is further removed from the fixed axis than for red. Hence the first median

Determination of true Optic Axial Angle of Cæsium Copper Sulphate.

Nature of light.	No. of section perp. 1st median line.	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.	{ 1	39° 3'	1a	115° 31'	43° 7'	43° 6'
	{ 2	38 55	2a	115 30	43 0	
	{ 3	39 6	3a	115 35	43 10	
C.	{ 1	39 4	1a	115 22	43 10	43 9
	{ 2	38 58	2a	115 22	43 4	
	{ 3	39 7	3a	115 27	43 12	
Na.	{ 1	39 8	1a	114 38	43 24	43 24
	{ 2	39 7	2a	114 40	43 22	
	{ 3	39 11	3a	114 45	43 25	
Tl.	{ 1	39 13	1a	113 47	43 40	43 40
	{ 2	39 16	2a	113 56	43 41	
	{ 3	39 15	3a	113 52	43 40	
F.	{ 1	39 21	1a	112 35	44 4	44 3
	{ 2	39 30	2a	113 0	44 7	
	{ 3	39 20	3a	112 52	43 59	

line is dispersed in such a manner that for red it is nearer to the morphological axis a than it is for blue; the amount indicated was about 20—25'. It is interesting to note that the only other salt of the series which exhibits this order of dispersion of the median lines is the cæsium magnesium salt, and that in both these cases this reversal of the usual order of dispersion for the series is accompanied by the exhibition of an exceptionally small optic axial angle, and near approach to coincidence of the α and β refractive indices.

Effect of Rise of Temperature on the Optic Axial Angle.—Section 2 was heated to 70°, at which temperature the apparent angle in air measured 66° 40' for sodium light. Hence 2E decreases about 1½° for 50° rise of temperature.

Refractive Indices.—Seven excellent prisms were ground upon four crystals, and furnished the results given in the accompanying table.

The β indices, corrected to a vacuum, are accurately represented, for any wave-length λ almost as far as G, by the formula

$$\beta = 1.4940 + \frac{417 \ 147}{\lambda^2} + \frac{580 \ 700 \ 000 \ 000}{\lambda^4} + \dots$$

The α indices are very closely reproduced if the constant 1.4940 is diminished by 0.0015, and the γ indices if it is increased by 0.0091. The relations of these two differences from β determine the sign of double refraction to be again positive.

Effect of Rise of Temperature on Refraction.—Determinations at 70° yielded refractive indices about 0.0016 lower than the values at the ordinary temperature.

Determination of Refractive Indices of Cæsium Copper Sulphate.

Index.	Nature of light.	Crystal 1, 1 prism.	Crystal 2, 2 prisms.	Crystal 3, 2 prisms.	Crystal 4, 2 prisms.	Mean refractive index.
α Vibrations parallel 2nd median line α	Li	—	1·5018	1·5017	1·5017	1·5017
	C	—	1·5022	1·5021	1·5020	1·5021
	Na	—	1·5049	1·5048	1·5047	1·5048
	Tl	—	1·5075	1·5074	1·5074	1·5074
	F	—	1·5109	1·5108	1·5107	1·5108
	G	—	1·5160	1·5155	1·5163	1·5159
β Vibrations parallel symmetry axis b β	Li	1·5030	1·5035	1·5033	1·5030	1·5032
	C	1·5034	1·5039	1·5037	1·5034	1·5036
	Na	1·5059	1·5064	1·5062	1·5060	1·5061
	Tl	1·5085	1·5091	1·5090	1·5089	1·5089
	F	1·5120	1·5126	1·5123	1·5122	1·5123
	G	1·5171	1·5175	1·5171	1·5179	1·5174
γ Vibrations parallel 1st median line γ	Li	1·5120	1·5125	1·5121	1·5122	1·5122
	C	1·5124	1·5128	1·5125	1·5126	1·5126
	Na	1·5151	1·5156	1·5153	1·5153	1·5153
	Tl	1·5179	1·5185	1·5178	1·5179	1·5180
	F	1·5215	1·5220	1·5213	1·5214	1·5216
	G	1·5268	1·5268	1·5266	1·5263	1·5266

Ratio of Axes of Optical Velocity Ellipsoid.—These ratios are as follows.

$$\alpha : \beta : \gamma = 1.0009 : 1 : 0.9939.$$

Molecular Optical Constants.—The values of these constants are tabulated below.

Ax's of optical ellipsoid	α .	β .	γ .
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n \dots$	{ C. 0.1035	0.1037	0.1053
	{ G. 0.1059	0.1061	0.1077
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m \dots$	{ C. 65.04	65.20	66.18
	{ G. 66.54	66.70	67.69
Specific dispersion, $n_G - n_C \dots$	0.0024	0.0024	0.0024
Molecular dispersion, $m_G - m_C \dots$	1.50	1.50	1.51
Molecular refraction, $\frac{n - 1}{d} M \dots$	C. 110.64	110.97	112.96

These values are substantially constant for all temperatures at which the salt is capable of existing, as refraction and density are similarly affected by change of temperature.

SALTS CONTAINING CADMIUM.

As stated in the former communication, efforts to prepare a potassium cadmium sulphate containing $6H_2O$ have proved unavailing.

Rubidium Cadmium Sulphate, $\text{Rb}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

The crystals of this salt exhibit a perfect *cleavage* parallel $r'\{\bar{2}01\}$, in common with the other salts of the series. Good images of the goniometer signal are obtained from the freshly cleaved surfaces, at exactly 180° from r' .

Considerable difficulty attended the investigation of this salt, on account of the unfortunate property referred to in the former memoir (p. 407), of efflorescing and becoming perfectly opaque with extreme rapidity after removal from the mother liquor.

Volume.

Relative Density.—In order to determine the density, the device was adopted of weighing the salt under carbon tetrachloride, the liquid used in the determinations. It had previously been found that benzene and carbon tetrachloride were both effective in preventing freshly grown crystals from losing their transparency for some considerable time, several days, as a rule. Four crops of beautifully perfect crystals were employed. In each case the crystals were rapidly dried on blotting paper as they were removed from the mother liquor, and then immediately placed under benzene. They were then well washed with several quantities of pure benzene, in order to remove the last traces of moisture. Two or three at a time were then removed, drained from benzene on blotting paper, given two minutes or so to lose the last traces of that liquid by evaporation, afterwards powdered as rapidly as possible in the agate mortar, and eventually transferred to the pyknometer, which already contained a known weight of carbon tetrachloride, sufficient to amply cover the powder; when sufficient had thus been introduced, the stopper and cap were replaced, the whole fixed in the wire spring stand, and weighed after the usual interval to permit of the surface equilibrium of the pyknometer being attained. A slight correction was made, in accordance with the indications of a duplicate experiment with the liquid alone, for the small amount of loss of carbon tetrachloride by evaporation during the transference of the salt to the pyknometer. The remaining small errors, due to a possible trace of moisture or benzene, on the one hand, and to slight efflorescence during the powdering, on the other, affect the density in opposite directions and thus tend to neutralise each other. The results obtained are as follows.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
4.2949	2.6726
2.5409	2.6712
3.8547	2.6677
3.0104	2.6744
Mean	2.6715

Perrot found the density about 2.70.

$$\text{Molecular Volume.}—\frac{M}{d} = \frac{582.4}{2.672} = 217.96.$$

Distance Ratios.—The axial angle β was previously shown to be $74^{\circ} 7'$, and the axial ratio

$$a : b : c = 0.7346 : 1 : 0.4931.$$

Combination of these with the molecular volume affords the following distance ratios.

$$\chi : \psi : \omega = 6.2828 : 8.5526 : 4.2174.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—The rapidity of efflorescence is such that section-plates or prisms ground as quickly as possible are absolutely opaque by the time they are completed. It was found possible, however, to obtain prisms sufficiently transparent for the purposes of the determinations of refractive index, by a device which will be described in connection with those determinations.

Five section-plates, parallel to the symmetry plane, were prepared with the greatest rapidity consistent with due care as to their orientation, using a cementing wax which remains soft just sufficiently long for the purpose after becoming moderately cool, in order to avoid hastening the efflorescence by rise of temperature; but all were useless when finished, having the appearance of white chalk. Attempts to obtain sections by cementing the first surface upon one of the glass discs intended for use with the special crystal holder employed for grinding a second parallel surface, by a cold viscid solution of hard balsam in benzene, covering the whole crystal with a protecting layer of the same, and then grinding the second surface after standing all night to harden, were also fruitless as opacity always supervened during the interval.

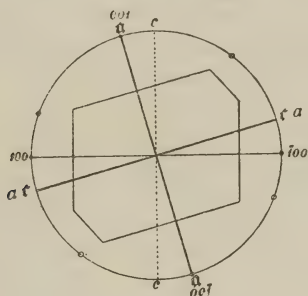
The orientation of the optical planes was, however, determined by immersion of transparent crystals, freshly removed from the mother liquor, in toluene, whose refractive index is nearly the same as the mean index of the crystal, contained in the cell of a stage goniometer, forming one of the accessories of a Swift petrological microscope. The crystal was arranged so that the symmetry plane lay parallel to the stage, and the edge (110):(010) was focussed and brought parallel to one of the spider lines, in order to utilise it as reference direction. The extinction angle made with this edge was then determined in the usual manner, and repeated with the crystal rotated 180° , in order to eliminate any error of parallelism between spider line and nicols. It was found in each case that extinction occurred at about 16° from this edge, and apparently exactly normal to the basal plane, that is, to the edge (001):(011). Now the com-

plement of the axial angle ($74^{\circ} 7'$) is $15^{\circ} 53'$, and this angle is the inclination between the reference edge and the normal to the basal plane. The difference between 16° and $15^{\circ} 53'$ is within the error of the determinations, so that the extinction is normal to the basal plane within the usual error of stauroscopical determinations.

Perrot arrived at the same conclusion, but does not state the method of determining it.

This direction is the second median line, and the first median line is the direction at right angles in the symmetry plane, as shown in Fig. 21.

FIG. 21.



The *sign of double refraction* is positive, proved by the relations of the refractive indices, and demonstrated by the quarter undulation mica. Hence the orientation is as follows.

The first median line ϵ is coincident with the morphological axis a .

The second median line a lies in the obtuse angle of the morphological axes ac , it is precisely normal to $c\{001\}$, and is inclined $15^{\circ} 53'$ to the vertical axis c .

The first median line is consequently inclined exactly 90° to the normal to $c\{001\}$, and $15^{\circ} 53'$ to the normal to $a\{100\}$.

The above method of determining extinctions, by immersion in a liquid of the same refractive index as the crystal, has lately been described by Klein (*Sitz. Ber., Berlin Akademie*, 1895, **5**, 91). The author has long been in the habit of having recourse to measurements in such liquids in difficult cases, and the present instance affords a good example of the value of the method. The refracting edges of the crystal in such a medium exert no disturbing influence on the observations, the crystal behaving like a parallel-sided plate.

Optic Axial Angle.—The method has been further utilised, as in the case of rubidium sulphate described in the 1894 memoir (p. 692), and the case of caesium magnesium sulphate described in the present communication, in order to determine the true optic axial angle of rubidium cadmium sulphate. Two liquids were employed, very

slightly lower and higher respectively than the mean index of the crystals, namely, turpentine and toluene, as in the case of the cæsium magnesium salt, whose indices are nearly the same as those of the salt now under consideration. The mean of the angles in the two liquids is considered as the true angle. As the second median line is perpendicular to the well-developed faces of the basal plane, the obtuse angle of the axes was actually observed. Fresh, perfectly transparent crystals, which had been well washed with benzene were taken and measured, first in toluene, which, being volatile, rapidly dries off the crystal after removal of the cell, and subsequently in turpentine. The results are presented in the accompanying table.

Determination of true Optic Axial Angle of Rubidium Cadmium Sulphate.

Nature of light.	No. of crystal.	Angle in toluene.	Angle in turpentine.	Mean values.	Mean obtuse angle.	Mean acute angle, $2Va$.
Li.....	{ 1	106° 30'	108° 48'	107° 39'	107° 40'	72° 20'
	{ 2	106 36	108 55	107 46		
	{ 3	106 33	108 35	107 34		
C	{ 1	106 28	108 48	107 38	107 39	72 21
	{ 2	106 35	108 55	107 45		
	{ 3	106 32	108 35	107 33		
Na.....	{ 1	106 16	108 46	107 31	107 34	72 26
	{ 2	106 27	108 54	107 40		
	{ 3	106 27	108 34	107 30		
Tl.....	{ 1	106 8	108 44	107 26	107 29	72 31
	{ 2	106 21	108 51	107 36		
	{ 3	106 21	108 32	107 26		
F	{ 1	105 56	108 41	107 18	107 23	72 37
	{ 2	106 14	108 49	107 31		
	{ 3	106 14	108 29	107 21		

Perrot determined the angle upon two natural plates parallel $\{20\bar{1}\}$, by the indirect method, and obtained the values $71^{\circ} 59'$ and $72^{\circ} 15'$ for sodium light.

Dispersion of the Median Lines.—The observations in both liquids indicated that the second median line is dispersed so that for blue it is nearer to the vertical axis of the crystal than for red, and that the first median line is correspondingly dispersed so that for blue it is nearer to the normal to $a \{100\}$ than it is for red. The amount of dispersion is about $10'$ between Li and F. The indications regarding the dispersion of the axes themselves are different in the two liquids, but the mean of the two sets of readings shows that both axes exhibit dispersion, but the one emerging between $r'\{20\bar{1}\}$ and $s'\{10\bar{1}\}$ least.

Measurements at higher temperatures were manifestly impossible with this salt.

Refractive Indices.—It happens fortunately that, in this salt, one of the principal planes, bc , of the optical ellipsoid is parallel to the basal plane, for this enables a pair of faces of the clinodome $q\{011\}$, which are symmetrical to the basal plane, and whose edge is parallel to the first median line, the optical elasticity axis c , to be utilised for the determination of the refractive indices β and γ . Three such crystals were employed, fresh, transparent individuals with largely developed q faces being chosen. In order to prevent efflorescence during the measurements, and also to eliminate the effects of any minute imperfections of the faces, the two faces utilised as a prism were in each case fitted with thin micro-cover glasses cemented by a solution of hard balsam in benzene. Four other prisms were obtained by grinding, in such directions as to afford the indices α and β . This was successfully achieved by choosing crystals of such shape that the wax of the crystal holder of the grinding instrument, while only slightly warm just before setting hard, could be attached to a part of the crystal sufficiently removed from the part where the prism faces were to be ground as not to exert any great influence in accelerating efflorescence; also, as soon as the necessary adjustment of the crystal had been achieved, by goniometrical observation of the reference faces, the part of the crystal projecting out of the wax was coated with the balsam solution, which retarded materially the efflorescence. Working quickly with these precautions, not waiting to polish the ground surfaces, cleaning the crystal from wax entirely by immersion in benzene, thickly coating the first ground prism face with balsam solution immediately on removing the crystal from the benzene, and finally, when the second face had been ground in like manner, without allowing the warm wax to approach dangerously near to the first face while attaching to the holder, the two surfaces were coated with balsam and fitted with cover glasses, and a prism thus obtained which, in each case, proved sufficiently transparent to afford clear refracted images of the spectrometer slit. One of these prisms was ground upon one of the three crystals previously used to determine β and γ .

The results afforded by the seven prisms are given in the accompanying table (p. 450).

The β index, corrected for a vacuum, is accurately expressed for any wave-length λ nearly as far as F by the following formula.

$$\beta = 1.4706 + \frac{602\ 672}{\lambda^2} - \frac{3\ 327\ 400\ 000\ 000}{\lambda^4} + \dots$$

The α index is very closely expressed by the formula if the constant 1.4706 is diminished by 0.0048, and the γ index if it is increased by 0.0100. The positive nature of the double refraction is

Determination of Refractive Indices of Rubidium Cadmium Sulphate.

Index.	Nature of light.	Crystal 1, 2 prisms.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.	Mean refrac- tive index.	Perrot's values.
α Vibrations parallel 2nd median line α .	Li	1.4774	—	1.4771	1.4773	1.4774	—	1.4773	—
	C	1.4778	—	1.4775	1.4777	1.4778	—	1.4777	1.4773
	Na	1.4798	—	1.4797	1.4797	1.4800	—	1.4798	1.4800
	Tl	1.4823	—	1.4821	1.4824	1.4825	—	1.4823	—
	F	1.4856	—	1.4854	1.4857	1.4859	—	1.4856	1.4856
	G	1.4906	—	—	—	—	—	1.4906	—
β Vibrations parallel symmetry axis b .	Li	1.4824	1.4816	1.4821	1.4826	1.4816	1.4820	1.4820	—
	C	1.4828	1.4820	1.4824	1.4829	1.4820	1.4824	1.4824	—
	Na	1.4852	1.4842	1.4849	1.4852	1.4844	1.4848	1.4848	1.4851
	Tl	1.4876	1.4868	1.4872	1.4876	1.4867	1.4872	1.4872	—
	F	1.4909	1.4900	1.4903	1.4909	1.4904	1.4905	1.4905	1.4908
	G	1.4955	—	—	—	—	—	1.4955	—
γ Vibrations parallel 1st median line ϵ .	Li	1.4923	1.4915	—	—	—	1.4919	1.4919	—
	C	1.4927	1.4919	—	—	—	1.4923	1.4923	—
	Na	1.4952	1.4943	—	—	—	1.4948	1.4948	1.4952
	Tl	1.4976	1.4969	—	—	—	1.4972	1.4972	—
	F	1.5012	1.5001	—	—	—	1.5008	1.5007	—
	G	1.5061	—	—	—	—	—	1.5061	—

proved by the fact that the former is the smaller of the two differences from β .

Determinations at higher temperatures were out of the question.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices afford the following ratios.

$$a : b : c = 1.0034 : 1 : 0.9933.$$

Molecular Optical Constants.—The calculated values of these constants are appended.

Axis of optical ellipsoid.....	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$..	{ C. 0.1060	0.1068	0.1087
	{ G. 0.1084	0.1093	0.1113
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$ {	C. 61.71	62.23	63.31
	G. 63.13	63.66	64.81
Specific dispersion, $n_G - n_C$	0.0024	0.0025	0.0026
Molecular dispersion, $m_G - m_C$	1.42	1.43	1.50
Molecular refraction, $\frac{n - 1}{d} M$	C. 104.21	105.23	107.39.

Cæsium Cadmium Sulphate, Cs₂Cd(SO₄)₂.6H₂O.

There is a good *cleavage* parallel $r'\{201\}$; the cleaved surfaces reflect perfect images of the goniometer signal at exactly 180° from r' .

Volume.

Relative Density.—The crystals of cæsium-cadmium sulphate are not nearly so unstable as those of the rubidium salt, but efflorescence does ensue, to some extent, in the course of a day or two when freely exposed to the air. In order to avoid error due to this, the powdered substance was weighed under carbon tetrachloride, as in the case of the rubidium salt. Four crops of freshly grown, perfectly transparent crystals, derived from two independent preparations, were employed for the density determinations, and yielded the following results.

Weight of salt employed.	Sp. gr. at $20^\circ/4^\circ$.
2.4589	2.9551
1.8953	2.9559
3.8114	2.9535
3.8658	2.9561

Mean 2.9552

$$\text{Molecular Volume.} \quad \frac{M}{d} = \frac{677.4}{2.955} = 229.24.$$

Distance Ratios.—The axial angle β was previously shown to be $72^\circ 49'$, and the ratio of the axes

$$a : b : c = 0.7259 : 1 : 0.4906.$$

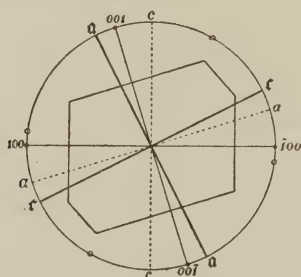
Combination of these with the molecular volume yields the following distance ratios.

$$\chi : \psi : w = 6.3638 : 8.7668 : 4.3010.$$

Optics.

Orientation of Axes of Optical Ellipsoid.—Transparent sections of this salt were successfully obtained by cementing the first ground face with solution of balsam upon one of the small glass discs furnished for use with the "parallel surface" crystal holder of the grinding instrument, covering the whole of the crystal with the balsam in order to retard efflorescence, allowing to stand all night to harden, and grinding the second surface next morning. Two section-plates parallel to the symmetry plane were thus obtained, and they each exhibited the extinction angle of $9^{\circ} 45'$ in front of the normal to $c\{001\}$, as represented in Fig. 22.

FIG. 22.



The *sign of double refraction* is positive, as demonstrated by means of a quarter undulation mica and proved by the relations of the three refractive indices. The morphological axial angle being $72^{\circ} 49'$, the orientation is as follows.

The first median line r lies in the acute angle of the morphological axes ac , and is inclined $9^{\circ} 45'$ to the axis a .

The second median line a lies in the obtuse angle ac , and is inclined $26^{\circ} 56'$ to the vertical axis c .

The first median line is also inclined $99^{\circ} 45'$ to the normal to $c\{001\}$, and $26^{\circ} 56'$ to the normal to $a\{100\}$.

Optic Axial Angle.—Three pairs of section-plates were obtained in the manner just described, and afforded the measurements given in the accompanying tables. Section 2 did not show the axes in air, being narrow in comparison with the considerable thickness required to afford fine brushes and small rings on account of the feeble double refraction.

Determination of the apparent Angle in Air of Cæsium Cadmium Sulphate.

Nature of light.	Section 1.	Section 3.	Mean 2E.
Li.....	114° 20'	114° 45'	114° 32'
C.....	114 15	114 40	114 27
Na.....	113 51	114 18	114 4
Tl.....	113 27	113 50	113 38
F.....	112 55	113 20	113 7

Determination of true Optic Axial Angle of Cæsium Cadmium Sulphate.

Nature of light.	No. of section perp. 1st median line	Observed values of 2Ha.	No. of section perp. 2nd median line.	Observed values of 2Ho.	Calculated values of 2Va.	Mean 2Va.
Li.....	{ 1	60° 58'	1a	97° 21'	68° 4'	68° 4'
	{ 2	60 36	2a	97 8	67 53	
	{ 3	60 55	3a	96 55	68 14	
C.....	{ 1	60 53	1a	97 17	68 2	68 2
	{ 2	60 32	2a	97 4	67 51	
	{ 3	60 50	3a	96 48	68 12	
Na.....	{ 1	60 30	1a	96 57	67 52	67 53
	{ 2	60 10	2a	96 45	67 42	
	{ 3	60 33	3a	96 30	68 6	
Tl.....	{ 1	60 4	1a	96 37	67 40	67 44
	{ 2	59 49	2a	96 20	67 35	
	{ 3	60 12	3a	96 11	67 57	
F.....	{ 1	59 25	1a	95 57	67 26	67 28
	{ 2	59 15	2a	95 50	67 20	
	{ 3	59 35	3a	95 43	67 39	

Monobromonaphthalene was used as immersion liquid for the determination of 2Ha and 2Ho. The order of dispersion was confirmed by observations in benzene, whose refractive index is near the mean index of the crystals, the angle being over half a degree larger for red than for blue.

Dispersion of the Median Lines.—The observations in benzene further indicated that the first median line was dispersed about 10—15', being nearer the morphological axis *a* for blue than for red. Both optic axes showed dispersion, the axis which emerges near the normal to *a*{100} much less than the other. The order is

red | blue blue | red.

No observations could be carried out at higher temperatures on account of the rapidity of decomposition.

Refractive Indices.—Six transparent prisms were successfully prepared on six different crystals by attaching the cementing wax of the crystal holder only to parts of the crystals removed from the portions where the surfaces were to be ground, and coating the first ground face thickly with balsam while the second surface was being

Determination of Refractive Indices of Cesium Cadmium Sulphate.

Index.	Nature of light.	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.	Mean refractive index.
α vibrations parallel 2nd median line, α .	Li	—	1.4947	1.4944	1.4950	1.4953	1.4943	1.4947
	C	—	1.4950	1.4946	1.4952	1.4957	1.4949	1.4951
	Na	—	1.4973	1.4970	1.4977	1.4982	1.4973	1.4975
	Tl	—	1.5000	1.4995	1.5001	1.5007	1.4998	1.5000
	F	—	1.5032	1.5027	1.5036	1.5039	1.5033	1.5033
	G	—	1.5080	1.5076	1.5083	1.5086	—	1.5081
β vibrations parallel symmetry axis b (b).	Li	1.4967	—	—	1.4977	—	1.4971	1.4972
	C	1.4971	—	—	1.4981	—	1.4976	1.4976
	Na	1.4997	—	—	1.5003	—	1.4999	1.5000
	Tl	1.5022	—	—	1.5030	—	1.5026	1.5026
	F	1.5054	—	—	1.5062	—	1.5057	1.5058
	G	—	—	—	1.5109	—	1.5103	1.5106
γ vibrations parallel 1st median line, ϵ .	Li	1.5029	1.5035	1.5030	—	1.5041	—	1.5034
	C	1.5033	1.5038	1.5034	—	1.5045	—	1.5038
	Na	1.5057	1.5064	1.5058	—	1.5068	—	1.5062
	Tl	1.5081	1.5091	1.5084	—	1.5096	—	1.5088
	F	1.5122	1.5124	1.5118	—	1.5129	—	1.5023
	G	—	1.5170	1.5168	—	1.5178	—	1.5172

ground. The prism faces were fitted with cover glasses as soon as the prisms were finished. The results are given in the accompanying table.

The β indices, corrected for a vacuum, are accurately expressed for any wave-length λ as far as F by the following formula.

$$\beta = 1.4876 + \frac{462\ 311}{\lambda^2} - \frac{621\ 000\ 000\ 000}{\lambda^4} + \dots$$

The α indices are very closely expressed by the formula if the constant 1.4876 is diminished by 0.0025, and the γ indices if it is increased by 0.0062. The former being the smaller difference from β , determines the sign of double refraction to be positive.

No observations at higher temperatures could be made on account of the rapid decomposition.

Ratio of Axes of Optical Velocity Ellipsoid.—The indices afford the following ratio.

$$a : b : c = 1.0017 : 1 : 0.9959.$$

Molecular Optical Constants.—The indices, combined with the density and molecular weight, give the following constants.

Axis of optical ellipsoid.	a.	b.	c.
Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$..	{ C. 0.0987	0.0992	0.1002
	{ G. 0.1010	0.1014	0.1025
Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m$	{ C. 66.91	67.19	67.91
	{ G. 68.39	68.67	69.42
Specific dispersion, $n_G - n_C$	0.0023	0.0022	0.0023
Molecular dispersion, $m_G - m_C$	1.48	1.48	1.51
Molecular refraction, $\frac{n - 1}{d} M$	C. 113.59	114.16	115.58

COMPARISON OF RESULTS.

It will be most convenient and instructive to make the comparison of the results, afforded for each property, for the whole of the 22 salts at once, in order that a general supervision of the changes brought about by the replacement of potassium by rubidium and the latter by cæsium in each of the eight sets may be obtained, and any modifications of such changes due to the influence of the second metal clearly exhibited.

Cleavage.

It has been found that—

The whole of the salts of the series exhibit a common cleavage direction, parallel to the orthodome $r'\{\bar{2}01\}$. The fracture is a very perfect one, exhibiting well-defined images of the goniometer signal at exactly 180° to r' .

Results of the Volume of Investigation.

Relative Density.—A comparative table of the densities found for the various salts is appended. The salts are arranged so that those containing the same alkali metal are vertically under each other, and with the second metals which they contain arranged in the order of their atomic weight. The differences between corresponding potassium and rubidium salts and rubidium and caesium salts are also shown.

Relative Densities of the Salts of the Series.

Second metal M contained.	Atomic weight of M.	Density of K salt.	Difference between K and Rb salts.	Density of Rb salt.	Difference between Rb and Cs salts.	Density of Cs salt.
Mg	24·0	2·028	0·354	2·382	0·288	2·670
Mn	55·0	—	—	2·459	0·279	2·738
Fe	56·0	2·169	0·347	2·516	0·275	2·791
Ni	58·9	2·233	0·350	2·583	0·282	2·865
Co	(Winkler.) 59·6	2·212	0·345	2·557	0·280	2·837
Cu	(Winkler.) 63·0	2·224	0·346	2·570	0·284	2·854
Zn	65·0	2·241	0·343	2·584	0·283	2·867
Cd	112·0	—	—	2·672	0·283	2·955

The following conclusions may be drawn from this table.

The increase in density brought about by the replacement of potassium by rubidium, and rubidium by caesium, is approximately constant for the particular change throughout the series. The difference evoked by the former change is larger than that produced by the latter in the proportion of almost exactly 5 : 4.

An increase in density usually accompanies the replacement of the second metal M by one of higher atomic weight. The nickel salts, however, do not fall in with this rule, being higher than the corresponding cobalt salts; this cannot be due to impurity in the nickel sulphate, for two different samples were employed in the preparation of each of the three salts, but no appreciable difference of density was detected; moreover, analyses of the double salts yielded almost theoretical results. A precisely similar fact is shown by the corresponding selenates containing potassium investigated by Topsøe and Christiansen. The sp. gr. of the potassium magnesium salt is given as 2·336, the potassium nickel salt 2·539, the potassium cobalt salt 2·514, the potassium copper salt 2·527, and the potassium zinc salt 2·538. Hence it must be a real property of the nickel salts. All these

differences due to the replacement of the second metal are much less in amount than those due to interchanges of the alkali metals.

The fact that the difference between the potassium and rubidium salts containing copper is about the average for the series, affords most satisfactory confirmation of the accuracy of the determinations of the density of the potassium salt, in connection with which unusual difficulties were experienced.

Molecular Volume.—A table is next given in which the molecular volumes are similarly compared.

Molecular Volumes of the Salts of the Series.

Second metal M contained.	Mol. vol. of K salt.	Difference between K and Rb salts.	Mol. vol. of Rb salt.	Difference between Rb and Cs salts.	Mol. vol. of Cs salt.	Difference between K and Cs salts.
Mg	198·23	9·33	207·56	13·19	220·75	22·52
Mn	—	—	213·66	12·93	226·59	—
Fe	200·09	9·13	209·22	13·42	222·64	22·55
Ni	195·65	9·27	204·92	12·99	217·91	22·26
Co	197·83	9·45	207·28	13·02	220·30	22·47
Cu	198·29	9·26	207·55	12·64	220·19	21·90
Zn	197·68	9·52	207·20	12·68	219·88	22·20
Cd	—	—	217·96	11·28	229·24	—

The most striking facts demonstrated by this table are the following.

An increase in volume occurs when potassium is replaced by rubidium or the latter metal by caesium. The amount of this increase is approximately constant throughout the series, the replacement of potassium by rubidium being invariably accompanied by an increase of about 9·3 units of volume, whilst the replacement of rubidium by caesium results in the relatively larger increase of about 13 units.

A similar relation is shown by the atomic volumes of the alkali metals themselves; thus the difference between the volume of rubidium (56·3) and potassium (45·5) is 10·8, whilst the difference between that of caesium (70·7) and of rubidium is 14·4.

The effect of the replacement of the second metal by another of different atomic weight cannot be expressed according to any such definite law. In the cases of the double salts containing magnesium, zinc, cobalt and copper the effect is almost nil, the molecular volumes of each set of salts containing the same alkali metal being almost the same. The salts containing iron and nickel, however, invariably exhibit molecular volumes about two units higher and lower respectively than the values for the four groups of salts just mentioned.

Topsøe and Christiansen also found that the corresponding potassium selenates containing magnesium, zinc, cobalt, and copper possessed almost identical molecular volumes, whilst the volume of the nickel salt was two units lower. In the cases of the members of the series containing manganese and cadmium, of which the double salts with potassium have not yet been prepared, considerably higher molecular volumes have been found. Indeed, it is not unlikely that this fact has something to do with the impracticability of bringing about the formation of the potassium manganese and potassium cadmium salts. The following statement expresses generally the facts regarding the influence of the second metal on the molecular volume.

The determination of the molecular volume is pre-eminently a function of the alkali metal R, change of the second metal M being usually accompanied by a relatively small change of volume. Thus, although the difference between the atomic weights of magnesium and either zinc or copper is nearly the same as that between either potassium and rubidium or rubidium and caesium, yet the maximum amount of alteration produced by interchange among the first three is less than 1 unit, whilst the amounts produced by interchange of the latter are as stated in the last rule, and when potassium is replaced by caesium the change of volume amounts to no less than 22 units.

The three nickel salts exhibit slightly lower and the iron salts slightly higher molecular volumes than do the salts containing magnesium, zinc, cobalt, and copper, whilst the salts containing manganese and cadmium exhibit abnormally large volumes, an observation which is probably connected with the fact that potassium manganous and potassium cadmium sulphate have not yet been found capable of preparation.

Distance Ratios.—We now approach the question of the relative distances apart, from centre to centre, of the structural units or groups of units of each set of three salts, along the directions of the three morphological axes.

In the accompanying table of comparison, in addition to the distance ratios actually afforded by the formulæ given in the introduction, the numbers for which were given in the description of each salt, there are also appended, on the right hand side, the numbers obtained by dividing out the values for all three salts by the value of ψ for the potassium salt, as was done in the case of the simple normal sulphates. The simpler numbers thus obtained will, of course, express the same relationship as the larger numbers.

It was shown in the communication concerning the morphology of the series that the morphological axial ratios are not capable of exhibiting very clearly the change of geometrical form on replacing one alkali metal by another, because of simultaneous and mutually neutralising changes in the facial angles which determine those

Comparative Table of Distance Ratios.

Salt.	χ	:	ψ	:	ω	or	χ	:	ψ	:	ω	
	Diff.		Diff.		Diff.		Diff.		Diff.		Diff.	
KMg	6.0881	:	8.2128	:	4.1006		0.7413	:	1	:	0.4993	
	1060		1577		637		129		192		78	
RbMg	6.1941	:	8.3705	:	4.1643		0.7542	:	1.0192	:	0.5071	
	837		2541		1014		102		309		123	
CsMg	6.2778	:	8.6246	:	4.2657		0.7644	:	1.0501	:	0.5194	
Total diff. ...	1897		4113		1651		231		501		201	
KZn	6.0618	:	8.1773	:	4.1247		0.7413	:	1	:	0.5044	
	978		1770		616		120		216		75	
RbZn	6.1596	:	8.3543	:	4.1863		0.7533	:	1.0216	:	0.5119	
	1002		2515		821		122		308		101	
CsZn	6.2598	:	8.6058	:	4.2684		0.7655	:	1.0524	:	0.5220	
Total diff. ...	1980		4285		1437		242		524		176	
KFe	6.0739	:	8.2336	:	4.1332		0.7377	:	1	:	0.5020	
	1093		1481		610		133		180		74	
RbFe	6.1832	:	8.3817	:	4.1942		0.7510	:	1.0180	:	0.5094	
	974		2680		900		118		325		109	
CsFe	6.2836	:	8.6497	:	4.2842		0.7628	:	1.0505	:	0.5233	
Total diff. ...	2067		4161		1510		251		505		183	
KNi	6.0342	:	8.1775	:	4.1051		0.7379	:	1	:	0.5020	
	872		1509		774		107		185		95	
RbNi	6.1214	:	8.3234	:	4.1825		0.7486	:	1.0185	:	0.5115	
	1075		2396		878		131		293		107	
CsNi	6.2289	:	8.5680	:	4.2703		0.7617	:	1.0478	:	0.5222	
Total diff. ...	1947		3905		1652		238		478		202	
KCo	6.0625	:	8.1881	:	4.1243		0.7404	:	1	:	0.5037	
	1093		1624		601		134		198		73	
RbCo	6.1718	:	8.3505	:	4.1844		0.7538	:	1.0198	:	0.5110	
	877		2596		931		107		318		114	
CsCo	6.2595	:	8.6101	:	4.2775		0.7645	:	1.0516	:	0.5224	
Total diff. ...	1970		4220		1532		241		516		187	
KCu	6.0893	:	8.1300	:	4.1366		0.7490	:	1	:	0.5088	
	1254		1674		361		154		206		45	
RbCu	6.2147	:	8.2974	:	4.1727		0.7644	:	1.0206	:	0.5133	
	1334		2476		536		164		304		65	
CsCu	6.3481	:	8.5450	:	4.2263		0.7808	:	1.0510	:	0.5198	
Total diff. ...	2588		4150		897		318		510		110	
RbMn	6.2542	:	8.4723	:	4.1938							
	899		2494		912							
CsMn	6.3441	:	8.7217	:	4.2850							
RbCd	6.2828	:	8.5526	:	4.2174							
	810		2142		826							
CsCd	6.3638	:	8.7668	:	4.3010							

ratios. It was observed, however, that in each set of three salts the ratios for the rubidium salt lay between those of the corresponding potassium and caesium salts. When, however, not only the change of geometrical form is considered, but also the change in the volume produced by the introduction of an alkali metal of greater atomic weight in the place of one of lower atomic weight, the differences exhibited are of so pronounced a character, as expressed by the numbers just tabulated, that the following important rules are at once recognised.

The replacement of potassium by rubidium or rubidium by caesium is accompanied by a marked increase in the separation of the centres of the structural units or groups of units along each of the axial directions, corresponding to the increase in volume. The distance ratios of any rubidium salt in the series are consequently intermediate between those of the potassium and caesium salts containing the same second metal. The amounts of increase when rubidium replaces potassium on the one hand, and when caesium replaces rubidium on the other, are approximately equal along the forward inclined axis a , but are considerably greater along both the lateral axis of symmetry b and the vertical axis c when caesium replaces rubidium than when the latter replaces potassium. As regards the relative amounts of increase along the directions of the three axes, the extension is invariably much the greatest along the axis of symmetry b , and least along the vertical axis c . Usually the extension along the latter direction does not fall much behind that along the inclined axis, but in the copper salts the individuality of that metal manifests itself in a considerable augmentation of the extension along the inclined axis at the expense of a corresponding decline of extension in the direction of the vertical axis.

If the relative amounts of extension of the axes are considered in relation to the initial relative lengths of the axes, which are approximately $0.75 : 1 : 0.5$, the amount along the axis of symmetry b is still found to predominate, being more in proportion to its length than in the cases of the other two directions.

Results of the Optical Investigation.

Orientation of the Axes of the Optical Ellipsoid.—The most convenient method of comparing the positions of the variable axes of the optical ellipsoid, which lie at right angles to each other in the symmetry plane, will be to tabulate the angles of inclination to the vertical morphological axis c of that axis of the ellipsoid which is not far removed from the normal to the basal plane $c\{001\}$. This direction has been shown throughout the whole series to be the maximum axis of the ellipsoid a , and it is the second median line in every case but that of caesium nickel sulphate, and the reason for that exception will presently be shown to be of a most interesting cha-

rafter. It is not so convenient to consider the inclinations of the first median line to the nearest morphological axis *a*, as it is sometimes on one side of that axis and sometimes on the other.

*Table of Inclinations of the Maximum Axis of the Optical Ellipsoid *a* to the Vertical Axis *c*.*

			Diff.				Diff.
KMg sulphate .	13° 38'			KZn sulphate..	10° 18'		
RbMg „ ..	21 14	7° 36'		RbZn „ ..	16 43	6° 25'	
CsMg „ ..	46 43	25 29		CsZn „ ..	30 16	13 33	
KFe „ ..	11 57	5 12		KNi „ ..	8 42	3 56	
RbFe „ ..	17 9	11 8		RbNi „ ..	12 38	11 29	
CsFe „ ..	28 17			CsNi „ ..	24 7		
KCo „ ..	10 5	5 56		KCu „ ..	18 33	7 55	
RbCo „ ..	16 1	10 7		RbCu „ ..	26 28	16 29	
CsCo „ ..	26 8			CsCu „ ..	42 57		
RbMn „ ..	16 57	8 30		RbCd „ ..	15 53	11 3	
CsMn „ ..	25 27			CsCd „ ..	26 56		

It will be apparent from this table that

*The orientation of the variable axes of the optical ellipsoid which lie in the symmetry plane, for every rubidium salt of the series, is intermediate between that for the potassium and that for the cæsium salt containing the same second metal. The maximum axis of the optical ellipsoid *a* lies nearest to the vertical morphological axis *c* in the case of the potassium salt of any group, and is furthest removed for the cæsium salt. The intermediate position for the rubidium salt is always considerably nearer to the position for the potassium salt than to that for the cæsium salt, the replacement of rubidium by cæsium being attended by a much greater change of orientation than in mere arithmetical proportion to the change in atomic weight.*

This important rule will be clearly demonstrated by the graphical representations of the orientations of the three salts of each group, given in Figs. 23—28 (p. 462).

The rule may be stated in a more interesting manner as follows.

*The optical ellipsoid rotates about its intermediate axis *b*, which is coincident with the morphological symmetry axis *b*, when one alkali metal is replaced by another. For any potassium salt of the series it is situated so that its major axis *a* is but slightly inclined to the vertical morphological axis *c*, in the obtuse axial angle *ac*; for the corresponding rubidium salt the inclination is greater in the same direction, and for the cæsium salt greater still, the difference of inclination in the latter case being much larger than in the former. The amount of rotation is thus much greater when cæsium replaces rubidium than when the latter metal replaces potassium.*

It is also observed that

The different chemical nature of copper, as compared with the other

FIG. 23.

Mg.

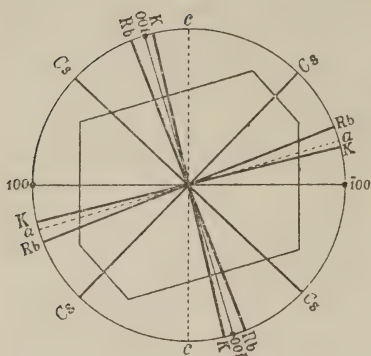


FIG. 24.

Zn.

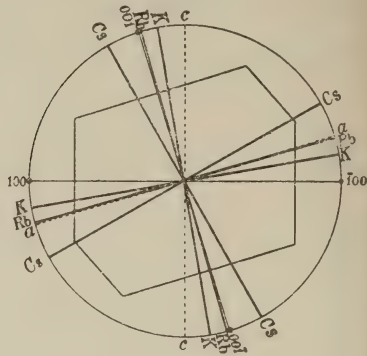


FIG. 25.

Fe.

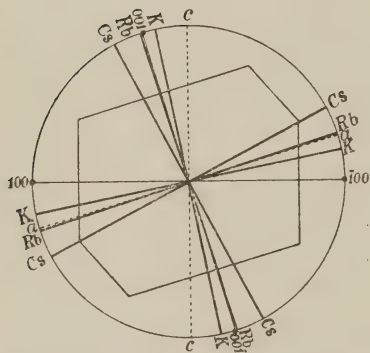


FIG. 26.

Ni.

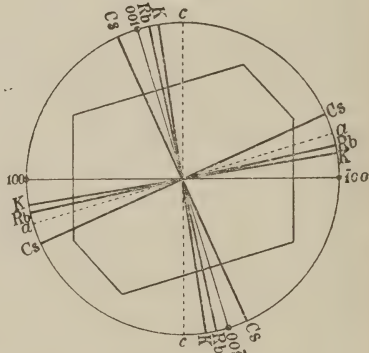


FIG. 27.

Co.

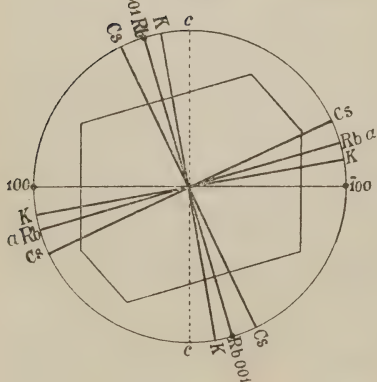
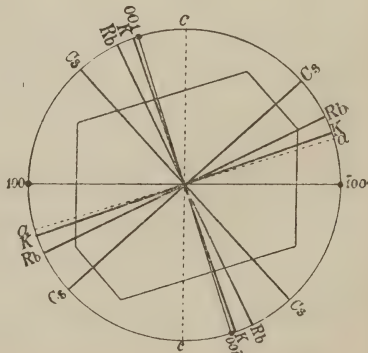


FIG. 28.

Cu.



second metals contained in the salts of the series, is again manifested by the fact that in the case of potassium copper sulphate the major axis a of the optical ellipsoid is inclined at so exceptionally large an angle to the vertical axis c as to be in front of the normal to the basal plane, whereas it is behind that normal in the other potassium salts of the series.

It will be most convenient to consider the refraction data before the optic axial angle phenomena in order that the latter may be more perfectly understood in the light of the refraction results.

Refractive Indices.—The accompanying tables (pp. 464 and 465) afford a comparison of the refractive indices of each of the eight sets of salts. It will be immediately observed that

The refractive indices of any rubidium salt of the series are, without exception, intermediate between those of the potassium and cesium salts containing the same second metal, and nearer to the values for the potassium salt.

The most accurate idea of the refraction relationships will be afforded by a comparison of the β indices. For the direction of vibration for the β indices is constant throughout the series, being the invariable axis of monoclinic symmetry b , whereas the directions within the crystals corresponding to the α and γ indices vary in accordance with the rule just formulated. As the difference in dispersion in the three salts of any set is so slight, it will be ample to compare the β values for sodium light, and this will be found to be more satisfactory than the consideration of the values for a so-called ray of infinite wave-length, afforded by the first constants of the formulæ expressing the refraction for any wave-length.

Table of β Indices for Sodium Light.

Salt.	β_{Na} .	Difference.	Salt.	β_{Na} .	Difference.
KMg	1.4629	60 } 229 169 }	KZn	1.4833	51 } 215 164 }
RbMg....	1.4689		RbZn....	1.4884	
CsMg....	1.4858		CsZn	1.5048	
KFe	1.4821	53 } 214 161 }	KNi	1.4916	45 } 213 168 }
RbFe	1.4874		RbNi	1.4961	
CsFe	1.5035		CsNi	1.5129	
KCo	1.4865	51 } 220 169 }	KCu	1.4864	42 } 197 155 }
RbCo	1.4916		RbCu	1.4906	
CsCo	1.5085		CsCu	1.5061	
RbMn....	1.4807	159	RbCd....	1.4848	152
CsMn	1.4966		CsCd	1.5000	

The following further conclusions may be drawn concerning the refractive indices after an inspection of the above table.

Comparison Table of Refractive Indices.

Index.	Nature of light.	Salts containing magnesium.			Salts containing zinc.			Salts containing iron.			Salts containing manganese.	
		K.	Rb.	Cs.	K.	Rb.	Cs.	K.	Rb.	Cs.	Rb.	Cs.
<i>a.</i>	Li	1.4581	1.4646	1.4828	1.4748	1.4307	1.4994	1.4731	1.4789	1.4976	1.4741	1.4918
	C	1.4585	1.4650	1.4832	1.4752	1.4811	1.4998	1.4735	1.4793	1.4980	1.4745	1.4922
	Na	1.4607	1.4672	1.4857	1.4775	1.4833	1.5022	1.4759	1.4815	1.5003	1.4767	1.4946
	Tl	1.4631	1.4695	1.4880	1.4797	1.4857	1.5047	1.4782	1.4839	1.5028	1.4791	1.4972
	F	1.4658	1.4724	1.4912	1.4826	1.4886	1.5079	1.4811	1.4870	1.5061	1.4821	1.5003
	G	1.4699	1.4762	1.4956	1.4866	1.4929	1.5125	1.4852	1.4916	1.5105	1.4864	1.5046
<i>β.</i>	Li	1.4603	1.4664	1.4830	1.4805	1.4856	1.5020	1.4795	1.4847	1.5007	1.4781	1.4936
	C	1.4607	1.4668	1.4834	1.4809	1.4860	1.5024	1.4799	1.4851	1.5011	1.4785	1.4940
	Na	1.4629	1.4689	1.4858	1.4833	1.4884	1.5048	1.4821	1.4874	1.5035	1.4807	1.4966
	Tl	1.4652	1.4713	1.4881	1.4857	1.4908	1.5073	1.4847	1.4898	1.5061	1.4831	1.4991
	F	1.4678	1.4743	1.4912	1.4889	1.4938	1.5104	1.4877	1.4929	1.5093	1.4860	1.5022
	G	1.4720	1.4782	1.4957	1.4929	1.4980	1.5151	1.4920	1.4973	1.5137	1.4907	1.5066
<i>γ.</i>	Li	1.4727	1.4755	1.4888	1.4938	1.4947	1.5064	1.4941	1.4949	1.5065	1.4890	1.4995
	C	1.4731	1.4759	1.4892	1.4942	1.4951	1.5068	1.4945	1.4953	1.5069	1.4884	1.4999
	Na	1.4755	1.4779	1.4916	1.4969	1.4975	1.5093	1.4969	1.4977	1.5094	1.4907	1.5025
	Tl	1.4778	1.4805	1.4940	1.4994	1.5001	1.5119	1.4995	1.5003	1.5121	1.4933	1.5051
	F	1.4810	1.4835	1.4970	1.5027	1.5033	1.5152	1.5028	1.5034	1.5153	1.4965	1.5083
	G	1.4853	1.4876	1.5015	1.5067	1.5078	1.5199	1.5071	1.5080	1.5198	1.5015	1.5129

Comparison Table of Refractive Indices.

Index.	Nature of light.	Salts containing nickel.			Salts containing cobalt.			Salts containing copper.			Salts containing cadmium.	
		K.	Rb.	Cs.	K.	Rb.	Cs.	K.	Rb.	Cs.	Rb.	Cs.
<i>a.</i>	Li	1·4809	1·4868	1·5061	1·4780	1·4833	1·5028	1·4807	1·4858	1·5017	1·4773	1·4947
	C	1·4813	1·4872	1·5065	1·4784	1·4837	1·5032	1·4811	1·4862	1·5021	1·4777	1·4951
	Na	1·4836	1·4895	1·5087	1·4807	1·4859	1·5057	1·4836	1·4886	1·5048	1·4798	1·4975
	Tl	1·4860	1·4920	1·5112	1·4830	1·4882	1·5079	1·4861	1·4912	1·5074	1·4823	1·5000
	F	1·4889	1·4949	1·5146	1·4861	1·4910	1·5112	1·4893	1·4943	1·5108	1·4856	1·5033
	G	1·4933	1·4996	1·5192	1·4904	1·4954	1·5159	1·4944	1·4991	1·5159	1·4906	1·5081
<i>β.</i>	Li	1·4889	1·4933	1·5100	1·4838	1·4889	1·5057	1·4834	1·4878	1·5032	1·4820	1·4972
	C	1·4893	1·4937	1·5104	1·4842	1·4893	1·5061	1·4838	1·4882	1·5036	1·4824	1·4976
	Na	1·4916	1·4961	1·5129	1·4865	1·4916	1·5085	1·4864	1·4906	1·5061	1·4848	1·5000
	Tl	1·4941	1·4987	1·5154	1·4889	1·4940	1·5110	1·4889	1·4933	1·5089	1·4872	1·5026
	F	1·4972	1·5017	1·5187	1·4919	1·4968	1·5142	1·4922	1·4966	1·5123	1·4905	1·5058
	G	1·5015	1·5062	1·5235	1·4961	1·5011	1·5188	1·4975	1·5013	1·5174	1·4955	1·5106
<i>γ.</i>	Li	1·5022	1·5023	1·5133	1·4973	1·4985	1·5102	1·4990	1·5007	1·5122	1·4919	1·5034
	C	1·5026	1·5027	1·5137	1·4977	1·4989	1·5106	1·4994	1·5011	1·5126	1·4923	1·5038
	Na	1·5051	1·5052	1·5162	1·5004	1·5014	1·5132	1·5020	1·5036	1·5153	1·4948	1·5062
	Tl	1·5077	1·5078	1·5189	1·5028	1·5038	1·5156	1·5047	1·5064	1·5180	1·4972	1·5088
	F	1·5109	1·5110	1·5221	1·5059	1·5068	1·5187	1·5081	1·5098	1·5216	1·5007	1·5023
	G	1·5153	1·5156	1·5266	1·5105	1·5114	1·5237	1·5134	1·5148	1·5266	1·5061	1·5172

An increase in the atomic weight of the contained alkali metal is accompanied by an increase in the refractive power of the crystal, and the increase in refraction becomes relatively greater, as the atomic weight becomes higher, than in mere numerical proportion to the increase of atomic weight. When the indices are considered, whose corresponding direction of vibration is constant throughout the series, being the invariable symmetry axis b , the amounts of increase due respectively to the replacement of potassium by rubidium, and of rubidium by caesium, vary slightly in the different sets, according to the nature of the second metal present, from 1 : 3 to 1 : 4.

The difference between the indices for the potassium and caesium salts of any group is not so large as was observed between those of the simple sulphates of potassium and caesium. In the latter case the difference of the β indices for sodium light amounted to 0.0697 whereas the largest difference in the series under consideration is 0.0229.

No relation can be traced between the atomic weight of the second metal present and the refractive indices. For instance, although there is a rise in refraction when magnesium is replaced by zinc, yet there is a fall again when the latter is replaced by cadmium.

Ratio of Axes of Optical Velocity Ellipsoid.—The difference of refraction along the three axes of the optical ellipsoid in any one salt, the modification of that difference on replacement of the alkali metal by another, and the actual change of refraction along any one direction brought about by the same cause, are perhaps most clearly rendered evident by a consideration of the axial ratios of the optical ellipsoid, which are relative measures of the velocity of light vibration along the three rectangular axes a , b , c , of the ellipsoid. The ratios given in the description of each salt are calculated with reference to the value along the b axis as unity. Such ratios, therefore, only express the relative facility for light vibration along the three axial directions of the particular salt in question. It was shown in the memoir concerning the simple normal sulphates (*loc. cit.*, 699) that by taking the value along the intermediate axis of the ellipsoid of the potassium salt as unity, and expressing all the other values for the set of three salts proportionately, the actual changes of velocity along all three axes on passing from a potassium to a rubidium salt, and from a rubidium to a caesium salt, are exhibited. In the ratios thus obtained for any set of three salts, those for the potassium salt are, of course, identical with those given in the descriptions, and those for the rubidium and caesium salts are obtained in each case by dividing the refractive index for sodium light, corresponding to the axis in question in that particular salt, into the β_{Na} index of the potassium salt.

The two series of ratios are given side by side in the accompanying table.

Ratios of the Axes of the Optical Velocity Ellipsoids of the Series.

Salt.	a.	b.	c.	or	a.	b.	c.
KMg.....	1·0015 3	: 1	: 0·9915 24		1·0015 44	: 1 41	: 0·9915 17
RbMg....	1·0012 11	: 1	: 0·9939 22		0·9971 124	: 0·9959 113	: 0·9898 90
CsMg....	1·0001	: 1	: 0·9961		0·9847	: 0·9846	: 0·9803
KZn.....	1·0039 5	: 1	: 0·9909 30		1·0039 39	: 1 34	: 0·9909 4
RbZn....	1·0034 17	: 1	: 0·9939 31		1·0000 126	: 0·9966 109	: 0·9905 77
CsZn.....	1·0017	: 1	: 0·9970		0·9874	: 0·9857	: 0·9828
KFe.....	1·0042 2	: 1	: 0·9901 30		1·0042 38	: 1 36	: 0·9901 5
RbFe....	1·0040 19	: 1	: 0·9931 30		1·0004 125	: 0·9964 106	: 0·9896 77
CsFe.....	1·0021	: 1	: 0·9961		0·9879	: 0·9858	: 0·9819
KNi.....	1·0054 10	: 1	: 0·9910 30		1·0054 40	: 1 30	: 0·9910
RbNi....	1·0044 16	: 1	: 0·9940 38		1·0014 127	: 0·9970 111	: 0·9909 71
CsNi....	1·0028	: 1	: 0·9978		0·9887	: 0·9859	: 0·9838
KCo.....	1·0039 1	: 1	: 0·9907 28		1·0039 35	: 1 34	: 0·9907 6
RbCo....	1·0038 19	: 1	: 0·9935 34		1·0004 132	: 0·9966 112	: 0·9901 78
CsCo.....	1·0019	: 1	: 0·9969		0·9872	: 0·9854	: 0·9823
KCu.....	1·0019 6	: 1	: 0·9896 18		1·0019 34	: 1 28	: 0·9896 10
RbCu....	1·0013 4	: 1	: 0·9914 25		0·9935 107	: 0·9972 103	: 0·9886 77
CsCu....	1·0009	: 1	: 0·9939		0·9878	: 0·9869	: 0·9809
RbMn...	1·0027 14	: 1	: 0·9933 28				
CsMn....	1·0013	: 1	: 0·9961				
RbCd....	1·0034 17	: 1	: 0·9933 26				
CsCd....	1·0017	: 1	: 0·9959				

In discussing the results afforded by the comparison of these ratios, it will be convenient to consider first the total change represented by the second series of ratios, and subsequently to revert to the effect of this change in modifying the mutual relations of the three axes of the optical ellipsoid of each salt, as exhibited by the first series of ratios.

FIG. 29. Mg.

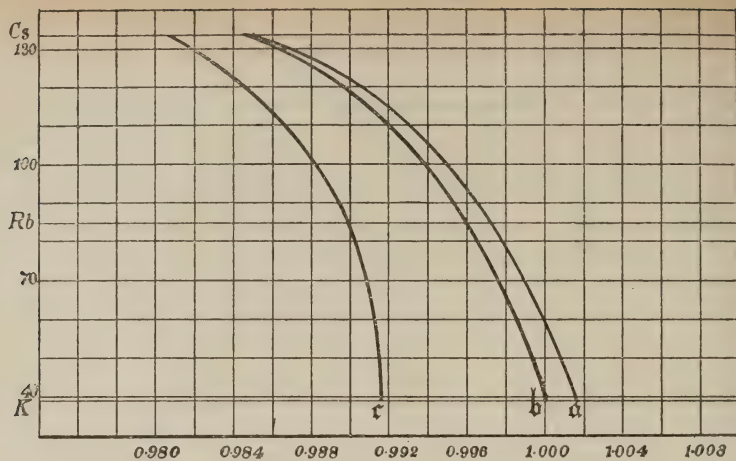


FIG. 30. Zn.

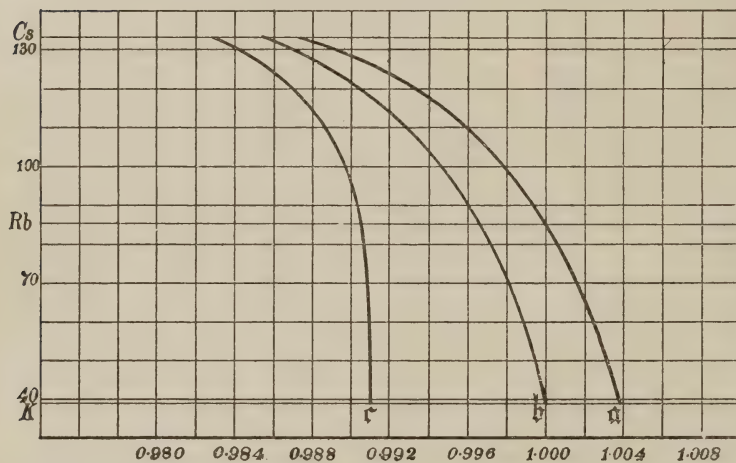


FIG. 31. Fe.

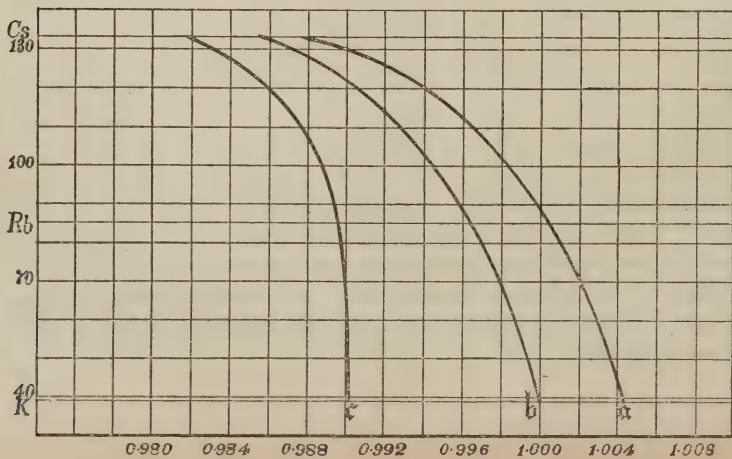


FIG. 32. Ni.

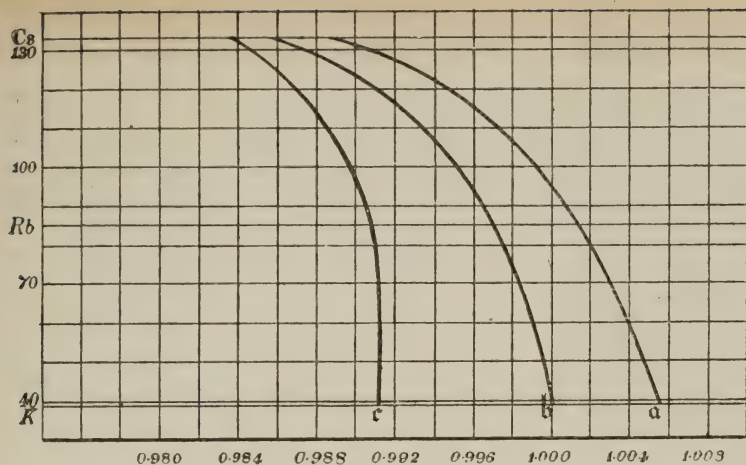


FIG. 33. Co.

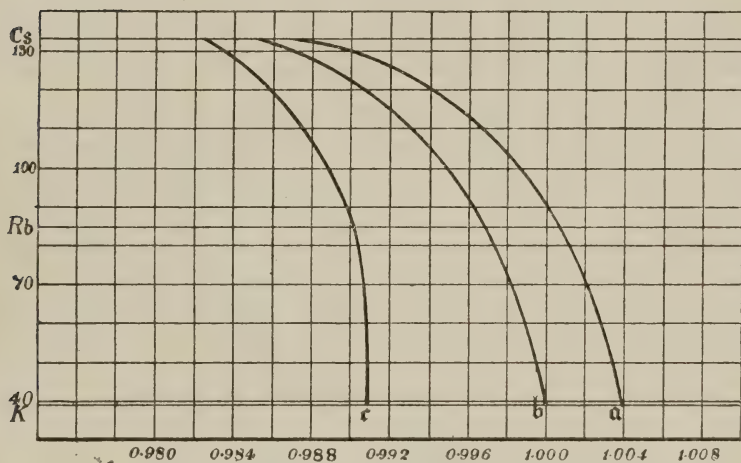
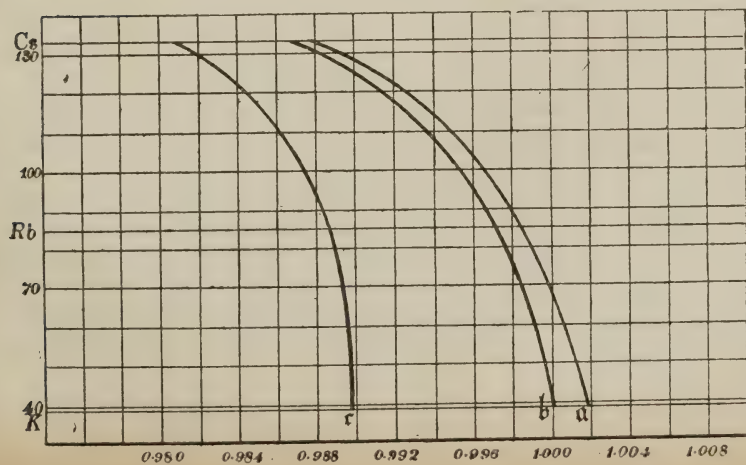


FIG. 34. Cu.



The second series reveal the following facts.

*The relative velocity of light vibration along each of the three axes of the optical ellipsoid of the crystals of every rubidium salt of the series is intermediate between the velocities along the corresponding axial directions in the crystals of the potassium and cæsium salts containing the same second metal. Increase in the atomic weight of the alkali metal is accompanied by a decrease in the velocity of light vibrations, or, in other words, by an increase of resistance to the vibration of light, along each of the axes of the ellipsoid, and this alteration is relatively much greater when cæsium replaces rubidium than when potassium is replaced by rubidium. In the case of the more strictly comparable direction of the invariable axis *b*, which is identical with the axis of morphological symmetry *b*, the relative amounts are as about 3 : 1. The amounts of change along the axis *a* are invariably slightly larger than those along the axis *b*, and in the same proportion; those along the axis *c* are always much less, and the difference between the effects respectively of replacing potassium by rubidium, and the latter by cæsium, is still more pronounced.*

It must be borne in mind that in the case of these monoclinic double sulphates the optical ellipsoid is not fixed as regards its axial directions, as in the case of the rhombic simple sulphates, but is rotatable about its intermediate axis *b*, coincident with the morphological symmetry axis *b*, as stated in one of the preceding rules. Hence the ellipsoid for a cæsium salt does not contain entirely within it the ellipsoid for the corresponding rubidium salt, and the latter in turn the ellipsoid for the analogous potassium salt, as was the case with the simple sulphates.

The relations of the various salts, as regards the vibration of light along the directions of the principal axes of the optical ellipsoid, are best exhibited graphically by means of curves. These are given in Figs. 29 to 34 for the six sets of salts whose three members are all capable of preparation. The atomic weight of the contained alkali metals is taken for ordinates and relative velocity of light vibration for abscissæ.

What is most apparent is the striking similarity of the curves, indicating unmistakably how little is the influence of the second metal in modifying the optical properties. The second point which attracts attention is the fact that in every case the curve takes a more or less steep course between the potassium and the rubidium salt, indicating the relatively small amount of change in the velocity on passing from one to the other, then rapidly curves to the left with diminishing steepness as it passes to the cæsium salt, indicating, in accordance with the rule above given, a much greater change when rubidium is replaced by cæsium. A third property common to the series is the

fact that the three curves of each set converge towards each other on passing from the potassium salt through the rubidium salt to the cæsium salt, indicating a progressive diminution in the amount of double refraction. Before enlarging on this last property, which leads to consequences of great interest, and only observing in passing how it ends in the case of the magnesium salts in the two nearest curves, those for the *a* and *b* axes, all but meeting, it will be advisable to discuss the first series of ratios.

The first series represent the relative velocities of light vibration along the three principal axes of the optical ellipsoid of each salt, compared with the value along the intermediate axis (the invariable axis of morphological symmetry) taken as unity. They further represent the net effect on the mutual relations of the axes of the progressive changes indicated by the second series. Now these mutual relations of the maximum, intermediate, and minimum velocities exclusively dominate the amount and the sign of the double refraction, and the optic axial angle, and it is for this reason that the discussion of the results of the observations of the latter have been deferred to a later stage, when these relations will have been made clear. In order that relations of such importance should be exhibited in the most striking manner, which is necessarily not achieved by the curves of Figs. 29 to 34 intended to demonstrate most clearly the properties referred to in preceding paragraphs, another series of curves are given in Figs. 35 to 40. In these curves the velocity along the intermediate axis is naturally always a vertical straight line representing unity. In every set the convergence of the curves for the two other axes is apparent. The curves corresponding to the axis *c* are in every case very nearly straight lines; those for the *a* axis exhibit more curvature, the amount of which varies somewhat according to the second metal present, but still the position of the rubidium salt is invariably an intermediate one. These observations lead to the following rule.

An increase in the atomic weight of the alkali metal is accompanied by convergence of the values of the velocity along the three axial directions abc towards unity, and consequently by a diminution in the amount of the double refraction. This property is already a very feeble one in the potassium salts, and is extremely weak in the cæsium salts, the rubidium salts occupying an intermediate position in this respect. The amounts of change in the velocity along the directions of the axes a and b, when potassium is replaced by rubidium or the latter metal by cæsium, being but slightly different, the relations of these two velocities are only slightly altered; the slower rate of change along the c axis, however, has the effect of introducing more considerable changes in the relations of the velocity along this direction to the velocities along the other two directions. Both the former slight relative alteration and the latter more consider-

FIG. 35. Mg.

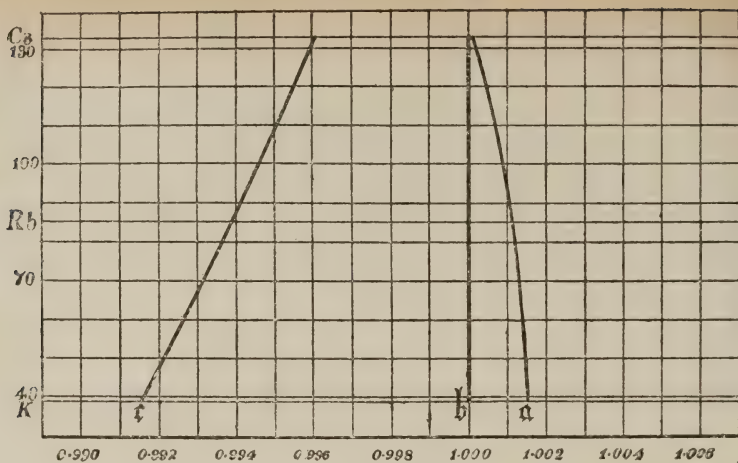


FIG. 36. Zn.

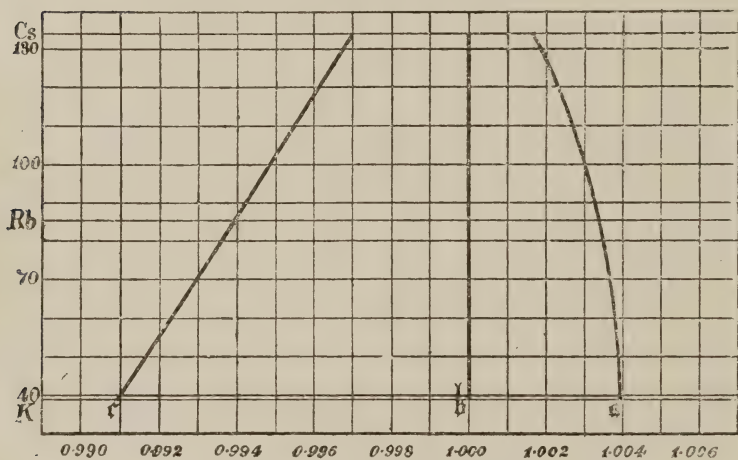


FIG. 37. Fe.

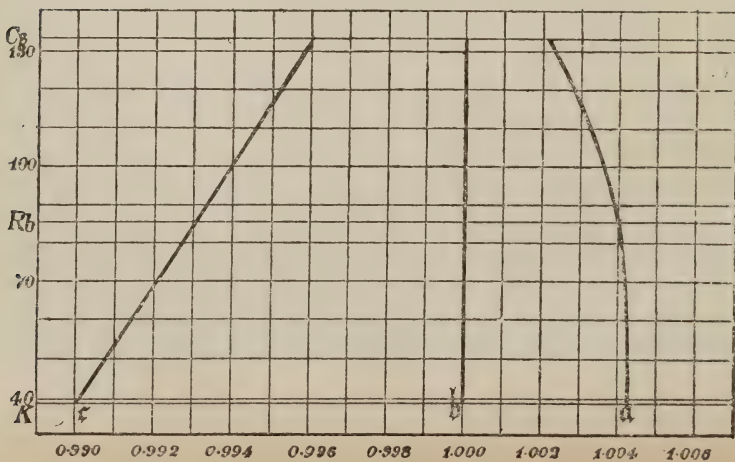


FIG. 38. Ni.

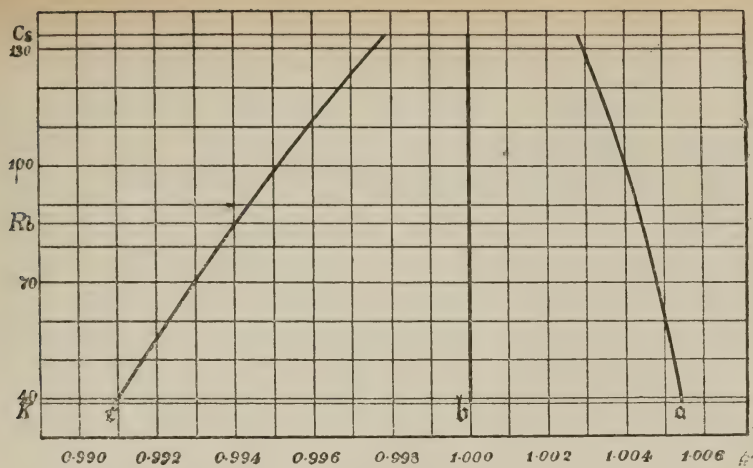


FIG. 39. Co.

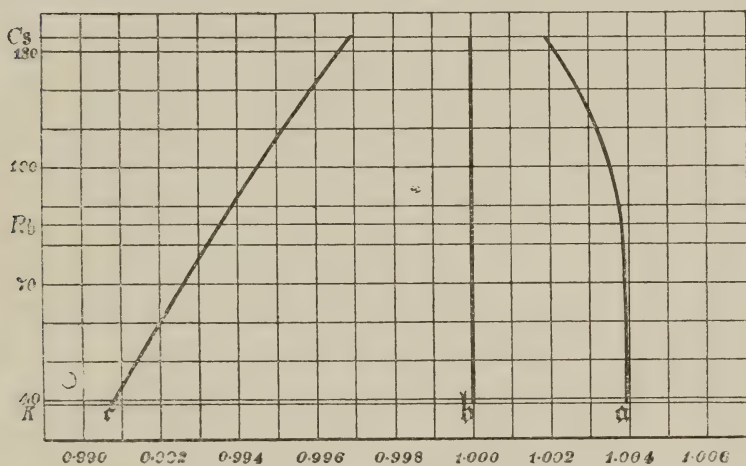
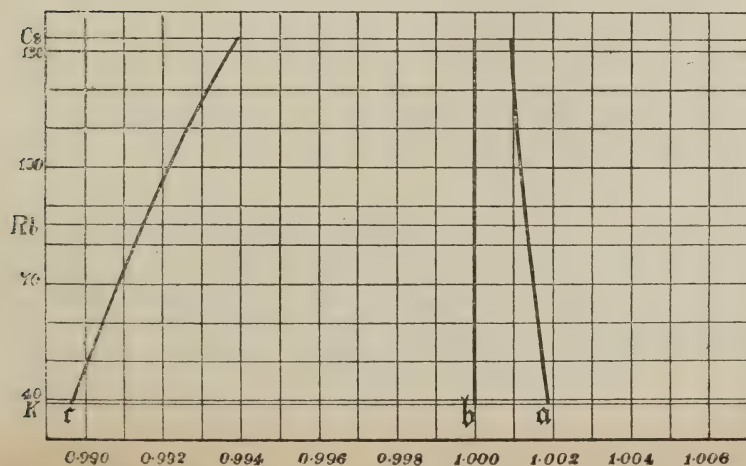


FIG. 40. Cu.



able one are progressive in character, the rubidium salts invariably occupying intermediate positions.

The bearing of this important rule on the individual refraction phenomena of the various salts of the series must next be discussed. It has been shown that the whole of the salts, with one exception, namely, caesium nickel sulphate, exhibit positive double refraction, that is, their β indices of refraction are nearer to the α values than to the γ values, and consequently the intermediate velocity ratios for the \mathbf{b} axis approach nearer to the maximum \mathbf{a} values than to the minimum \mathbf{c} values. This is evident from the table of ratios, and also from the curves of both series, the \mathbf{a} and \mathbf{b} curves lying closer together than the \mathbf{b} and \mathbf{c} curves.

In the exceptional case of caesium nickel sulphate, the β and γ refractive indices and the \mathbf{b} and \mathbf{c} ratios and curves approximate more closely to each other than do the α and β indices and the \mathbf{a} and \mathbf{b} ratios and curves, and therefore the sign of double refraction is negative. This apparent anomaly, instead of being an inexplicable exception, is a direct consequence of the operation of the rule last laid down, and is one of the most remarkable proofs of the validity of the rule which could be adduced. On inspection of the curves of either series, Figs. 32 or 38, for the salts containing nickel, it will be observed that for the potassium salt the \mathbf{a} and \mathbf{b} values, forming the starting points of their respective curves, are nearer together than the \mathbf{b} and \mathbf{c} values, and that at the rubidium salt the progress of the convergence of the curves still leaves them bearing similar relations, corresponding to a positive sign of double refraction. Now the potassium nickel salt presents greater divergence of the \mathbf{a} and \mathbf{b} values than any other salt of the series, as will be perhaps best seen by referring to the first series in the table of ratios, \mathbf{a} being here at its maximum with a value of 1.0054. Remembering that the relative change is more considerable along the \mathbf{c} axis, represented by more rapid convergence of its curve in Fig. 38, it is not surprising that, as the \mathbf{a} curve starts in the potassium salt further from \mathbf{b} than usual, it should, owing to its lesser rate of convergence, arrive at the caesium salt with a value further removed from \mathbf{b} than does the rapidly converging \mathbf{c} curve. This is indeed the case, and the reversal of the double refraction is due entirely to the operation of the rule. It may therefore be stated that

The preceding rule receives somewhat remarkable confirmation in the case of caesium nickel sulphate. With the exception of this salt, the whole of the salts of the series exhibit positive double refraction. Owing to the fact that in the potassium nickel salt the \mathbf{a} and \mathbf{b} values are at their maximum amount of removal for the series, although still nearest together of all the three values in accordance with positive double refrac-

tion, the precise operation of the rule causes it to happen that in the caesium salt the ϵ value, in consequence of its more rapid rate of convergence, has approached nearest the intermediate value \mathfrak{b} , and so this salt ought to exhibit negative double refraction, a presumption in complete accord with actual observation.

Just as the salts containing nickel exhibit a remarkable effect of the operation of the rule on account of the initial potassium salt exhibiting an unusually large divergence of the velocities along \mathfrak{a} and \mathfrak{b} , so the magnesium salts present another extraordinary effect of the rule, on account of the potassium salt presenting a particularly low difference of the values along the same two directions. For the effect of still further diminution in this difference, in accordance with the rule of convergence towards unity, results in the values of the velocities along the \mathfrak{a} and \mathfrak{b} axes actually arriving at unity in the caesium salt, as is graphically exhibited by the curves, Figs. 29 and 35.

It has been shown in the description of the caesium magnesium salt that the α and β refractive indices afforded by light vibrating parallel to \mathfrak{a} and \mathfrak{b} are almost identical; they differ by about two units in the fourth place of decimals for the red end of the spectrum, by one unit for sodium light, corresponding to the difference of the same amount shown in the ratios, which were calculated for sodium light, but are identical when expressed to four places for F light, and are absolutely identical for the wave-length 450 in the blue. Beyond this they again diverge, so that for G light they differ by one unit in the fourth decimal place, but the direction in the crystal which was formerly the maximum \mathfrak{a} axis is now the intermediate \mathfrak{b} axis, and yields the intermediate refractive index β . Hence the crystals of caesium magnesium sulphate yield only two refractive indices in blue light, simulating uniaxial optical properties; and for other colours it requires a spectrometer eye-piece of high power to detect any separation of the refracted images of the slit furnished by prisms affording vibrations parallel to the \mathfrak{a} and \mathfrak{b} axes. When such an eye-piece is employed, the images are observed to approach each other as the illuminating light changes from red towards the other end of the spectrum; they actually coincide when blue is reached, then pass each other, and again separate slightly on opposite sides of each other as their colour changes to violet. Moreover, the operation of the rule of convergence causes the third value ϵ to be comparatively near to the other values, thus rendering the double refraction extremely feeble. These remarkable effects of the rule in the case of caesium magnesium sulphate will be further followed when the optic axial angle phenomena, which are bound to be correspondingly extraordinary, are discussed. The facts as regards the refraction phenomena may be summarised as follows.

Another extraordinary effect of the operation of the rule is afforded by the refraction phenomena of *cæsium magnesium sulphate*. The differences between the *a* and *b* values is at its minimum for the potassium salts of the series in the case of *potassium magnesium sulphate*, and the rule of convergence towards unity results in the ratio *a* : *b* actually arriving at unity for the *cæsium* salt. Owing to the existence of the usual slight difference in dispersion along the axial directions, the coincidence is only absolute for wave-length 450 in the blue. The difference of the two velocities, or of the corresponding refractive indices, is about 0.0001 for Na and 0.0002 for Li light, the order being as usual throughout the series; for G light the values also differ by about 0.0001, but the order is reversed. These amounts are so slight that the pair of images of the spectrometer slit refracted by a 60° prism formed by faces having the directions theoretically required to yield these indices, are apparently coincident unless an eye-piece of very high power is employed. Hence for wave-length 450 *cæsium magnesium sulphate* exhibits apparent uniaxial optical properties.

It is further to be remarked that the influence of the second metal is only appreciably perceptible in the ratio *a* : *b*, best seen in the first series of ratios, the ratio *c* : *b* remaining substantially constant throughout the whole series of salts. No definite relation is remarked between the values of *a* : *b* in the groups of salts containing the same alkali metal, just as was remarked concerning the refractive indices themselves. As has just been shown, however, in the cases of the salts containing magnesium and nickel, although the specific effects on the ratio *a* : *b*, due to the second metal, are not connected by any rule involving only the atomic weight of that metal, those specific modifications are of very considerable importance in determining the optical phenomena presented by the crystals.

Molecular Optical Constants.—In the accompanying tables (pp. 478, *et seq.*), the optical constants, calculated by use of the formulæ of Lorenz and of Gladstone and Dale, are compared. The following facts are indicated by them.

The whole of the specific and molecular optical constants for any rubidium salt of the series are intermediate between those of the potassium and *cæsium* salts containing the same second metal.

The replacement of potassium by rubidium, and of the latter metal by *cæsium*, is accompanied by a diminution of specific refraction and specific dispersion, the amount of which is about twice as great when the former chemical change occurs as when the latter substitution is effected. The maximum amount of diminution in specific refraction occurs in the direction of the axis *c* of the optical ellipsoid; the somewhat smaller amounts of diminution along the directions *a* and *b* are almost identical, the

amount along the axis *b* being invariably, however, slightly the larger of the two.

The same chemical changes, involving an increase in the atomic weight of the alkali metal, are attended by an increase of molecular refraction and dispersion, the amount of which is greatest when cæsium replaces rubidium, the proportions for the two changes in molecular refraction being as 3 : 5. The amounts of increase of molecular refraction are nearly the same in the directions of the axes *a* and *b*, that along the former direction is slightly the greater, and is the maximum increase; the minimum increase occurs in the direction of the axis *c*. This rule is equally valid whatever may be the wave-length for which the comparison is made, and whether the constants are calculated by the formulæ of Lorenz or of Gladstone and Dale; moreover, as refraction and density are similarly affected by change of temperature within the limits between which the salts are capable of existing, it is independent of temperature.

With regard to the latter statement, it may be remarked that the main object of the determinations of refractive index at higher temperatures, recorded in the descriptions of the various salts, was to prove this point. In every case a rise of temperature was found to be accompanied by a lowering of the refractive index, the amount for 50° rise of temperature varying from 0·0012 to 0·0020.

The relations just established concerning the molecular refraction are in complete accordance with those set forth in a previous rule regarding the relative velocity of light vibration, as deduced from the second series of velocity ratios.

It is to be remarked that similar relations are exhibited by the refraction equivalents of the alkali metals themselves. The difference between the refraction equivalents of rubidium (10·5) and potassium (7·8) is 2·7, whilst that between the equivalents of cæsium (15·3) and rubidium is 4·8. The values taken for the equivalents are those deduced by the author from the comparison of the results of the two investigations concerning the simple and double sulphates, as described in the next communication.

The influence of the second metal in bringing about changes in the molecular optical constants is but slight compared with that due to the alkali metal. It is, however, perceptible in the case of the three more intimately related metals magnesium, zinc, and cadmium. If the rubidium or the cæsium salts containing respectively these three second metals are compared, it will be observed that: *The specific refraction diminishes when magnesium is replaced by zinc, and again when zinc is replaced by cadmium, whilst the molecular refraction increases under the same circumstances. The amount of the change is greatest, in the case of the specific refraction, when magnesium is replaced by zinc, and, in the case of the*

Table of Specific Refractions and Dispersions (Lorenz).

Salt.	Specific refraction, $\frac{n^2 - 1}{(n^2 + 2)d} = n$.						Specific dispersion. $n_D - n_C$.		
	For ray C (H α).			For ray G (H γ).			n.	h.	c.
	n.	h.	c.	n.	h.	c.			
KMg	0·1348 187	0·1353 188	0·1385 200	0·1377 192	0·1382 192	0·1415 205	0·0029	0·0029	0·0030
RbMg	·1161 90	·1165 94	·1185 103	·1185 91	·1190 96	·1210 105	·0024	·0025	·0025
CsMg	·1071	·1071	·1082	·1094	·1094	·1105	·0023	·0023	·0023
KZn	·1258 156	·1271 159	·1301 171	·1283 158	·1298 163	·1328 174	·0025	·0027	·0027
RbZn	·1102 76	·1112 81	·1130 92	·1125 77	·1135 82	·1154 93	·0023	·0023	·0024
CsZn	·1026	·1031	·1038	·1048	·1053	·1061	·0022	·0022	·0023
KFe	·1296 168	·1310 170	·1344 184	·1323 170	·1339 175	·1373 187	·0027	·0029	·0029
RbFe	·1128 77	·1140 83	·1160 93	·1153 80	·1164 85	·1186 96	·0025	·0024	·0026
CsFe	·1051	·1057	·1067	·1073	·1079	·1090	·0022	·0022	·0023
KNi	·1276 161	·1294 167	·1324 179	·1303 164	·1321 170	·1352 183	·0027	·0027	·0028
RbNi	·1115 76	·1127 82	·1145 94	·1139 78	·1151 83	·1169 96	·0024	·0024	·0024
CsNi	·1039	·1045	·1051	·1061	·1068	·1073	·0022	·0023	·0022
KCo	·1282 163	·1295 165	·1325 176	·1309 167	·1322 169	·1354 181	·0027	·0027	·0029
RbCo	·1119 76	·1130 82	·1149 93	·1142 77	·1153 83	·1173 94	·0023	·0023	·0024
CsCo	·1043	·1048	·1056	·1065	·1070	·1079	·0022	·0022	·0023
KCu	·1281 163	·1287 165	·1322 175	·1311 168	·1318 170	·1353 179	·0030	·0031	·0031
RbCu	·1118 83	·1122 85	·1147 94	·1143 84	·1148 87	·1174 97	·0025	·0026	·0027
CsCu	·1035	·1037	·1053	·1059	·1061	·1077	·0024	·0024	·0024
RbMn	·1145 84	·1153 89	·1173 93	·1169 86	·1178 91	·1200 102	·0024	·0025	·0027
CsMn	·1061	·1064	·1075	·1083	·1087	·1098	·0022	·0023	·0023
RbCd	·1060 73	·1068 76	·1087 85	·1084 74	·1093 79	·1113 83	·0024	·0025	·0026
CsCd	·0987	·0992	·1002	·1010	·1014	·1025	·0023	·0022	·0023

Table of Molecular Refractions and Dispersions (Lorenz).

Salt.	Molecular refraction, $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = m.$						Molecular dispersion. $m_D - m_C.$		
	For ray C (H α).			For ray G (H γ).			$\alpha.$	$\beta.$	$\gamma.$
	$\alpha.$	$\beta.$	$\gamma.$	$\alpha.$	$\beta.$	$\gamma.$			
KMg	54·18 3·24	54·40 3·21	55·66 2·91	55·34 3·26	55·55 3·27	56·88 2·92	1·16	1·15	1·22
RbMg	57·42 5·69	57·61 5·54	58·57 5·21	58·60 5·89	58·82 5·68	59·80 5·34	1·18	1·21	1·23
CsMg	63·11	63·15	63·78	64·49	64·50	65·14	1·38	1·35	1·36
KZn	55·72 3·30	56·29 3·24	57·61 2·87	56·86 3·39	57·48 3·30	58·84 2·95	1·14	1·19	1·23
RbZn	59·02 5·67	59·53 5·45	60·48 4·98	60·25 5·83	60·78 5·58	61·79 5·09	1·23	1·25	1·31
CsZn	64·69	64·98	65·46	66·08	66·36	66·88	1·39	1·38	1·42
KFe	56·22 3·18	56·87 3·15	58·34 2·75	57·41 3·29	58·09 3·21	59·60 2·81	1·19	1·22	1·26
RbFe	59·40 5·91	60·02 5·63	61·09 5·20	60·70 5·99	61·30 5·74	62·41 5·30	1·30	1·28	1·32
CsFe	65·31	65·65	66·29	66·69	67·04	67·71	1·38	1·39	1·42
KNi	55·75 3·25	56·54 3·13	57·84 2·75	56·93 3·34	57·73 3·21	59·06 2·84	1·18	1·19	1·22
RbNi	59·00 5·84	59·67 5·59	60·59 5·02	60·27 5·93	60·94 5·72	61·90 5·09	1·27	1·27	1·31
CsNi	64·84	65·26	65·61	66·20	66·66	66·99	1·36	1·40	1·38
KCo	56·08 3·23	56·66 3·24	58·00 2·89	57·28 3·25	57·84 3·28	59·26 2·92	1·20	1·18	1·26
RbCo	59·31 5·88	59·90 5·61	60·89 5·11	60·53 6·04	61·12 5·77	62·18 5·23	1·22	1·22	1·29
CsCo	65·19	65·51	66·00	66·57	66·89	67·41	1·38	1·38	1·41
KCu	56·48 3·17	56·75 3·11	58·30 2·90	57·81 3·18	58·11 3·11	59·68 2·93	1·33	1·36	1·38
RbCu	59·65 5·39	59·86 5·34	61·20 4·98	60·99 5·55	61·22 5·48	62·61 5·08	1·34	1·36	1·41
CsCu	65·04	65·20	66·18	66·54	66·70	67·69	1·50	1·50	1·51
RbMn	60·14 5·67	60·58 5·43	61·65 5·03	61·43 5·78	61·89 5·54	63·04 5·10	1·29	1·31	1·39
CsMn	65·81	66·01	66·68	67·21	67·43	68·14	1·40	1·42	1·46
RbCd	61·71 5·20	62·23 4·96	63·31 4·60	63·13 5·26	63·66 5·01	64·81 4·61	1·42	1·43	1·50
CsCd	66·91	67·19	67·91	68·39	68·67	69·42	1·48	1·48	1·51

molecular refraction, when zinc is replaced by cadmium, just as was observed on replacement of the alkali metal.

Table of Molecular Refractions (Gladstone and Dale), $\frac{n-1}{d} M$,
for Ray C.

Salt.	α .	Diff.	β .	Diff.	γ .	Diff.
KMg...	90.97		91.40		93.86	
RbMg...	96.60	5.63	96.97	5.57	98.86	5.00
CsMg...	106.76	10.16	106.80	9.83	108.08	9.22
KZn....	94.02		95.14		97.77	
RbZn...	99.77	5.75	100.78	5.64	102.67	4.90
CsZn....	109.98	10.21	110.56	9.78	111.52	8.85
KFe....	94.82		96.10		99.03	
RbFe...	100.36	5.54	101.58	5.48	103.71	4.63
CsFe....	111.01	10.65	111.70	10.12	112.99	9.28
KNi....	94.25		95.81		98.42	
RbNi...	99.92	5.67	101.25	5.44	103.09	4.67
CsNi....	110.46	10.54	111.31	10.06	112.03	8.94
KCo....	94.72		95.87		98.54	
RbCo...	100.34	5.62	101.50	5.63	103.49	4.95
CsCo....	110.95	10.61	111.58	10.08	112.57	9.08
KCu....	95.48		96.01		99.11	
RbCu...	100.99	5.51	101.41	5.40	104.09	4.98
CsCu...	110.64	9.65	110.97	9.56	112.96	8.87
RbMn..	101.47		102.32		104.44	
CsMn...	111.62	10.15	112.03	9.71	113.36	8.93
RbCd...	104.21		105.23		107.39	
CsCd...	113.59	9.38	114.16	8.93	115.58	8.19

Optic Axial Angle.—Having ascertained the facts concerning the refraction of the various salts of the series, and the relations of the velocity of light vibration along the principal axes of the optical ellipsoid of each salt, the study of the optic axial angle phenomena may now be approached with greatest advantage. In the accompanying table are set forth the values of the true optic axial angle, $2Va$, within the crystal, for the various salts of the series, arranged so that the potassium, rubidium, and caesium salts containing the same second metal may be readily compared. The following facts will be apparent.

Excluding the three salts containing magnesium, the caesium salt of which is not strictly comparable with the other two salts owing to the extraordinary conditions, previously described, following the operation of the rule regarding the velocity ratios, the optic axial angle of any rubidium salt of the series is intermediate between the optic axial angles of the potassium and caesium salts containing the same second metal, whatever wave-length of light is chosen for the comparison.

This rule is connected with the second rule established in connection with the velocities along the axial directions of the optical ellipsoid, the

progressive nature of the change there referred to leading to a progressive change in the optic axial angle, which varies in character in the different groups according to the relative rates of convergence of the extreme values of the velocity towards the intermediate value on passing from the potassium salt to the caesium salt of any group.

This variation in the character of the progressive change in the optic axial angle is due to the influence of the second metal.

Comparison Table of true Optic Axial Angles, 2Va.

Nature of light.	CsMg salt (not compar- able, special circum- stances).						KZn salt.	RbZn salt.	CsZn salt.			
	KMg salt.		RbMg salt.									
Li.	48°	0'	49°	6'	18°	10'	68°	17'	73°	42'	74°	30'
C.	47	59	49	2	18	0	68	16	73	40	74	27
Na.	47	54	48	46	16	25	68	14	73	33	74	11
Tl.	47	48	48	29	14	20	68	12	73	27	73	52
F.	47	40	48	10	11	15	68	9	73	18	73	31
	KFe salt.		RbFe salt.		CsFe salt.		KNi salt.	RbNi salt.	CsNi salt.			
Li.	67°	1'	73°	24'	75°	2'	75°	21'	82°	5'	92°	45'
C.	67	2	73	23	75	0	75	19	82	4	92	43
Na.	67	7	73	21	74	51	75	16	82	0	92	39
Tl.	67	12	73	18	74	42	75	13	81	56	92	31
F.	67	19	73	13	74	31	75	9	81	48	92	20
	KCo salt.		RbCo salt.		CsCo salt.		KCu salt.	RbCu salt.	CsCu salt.			
Li.	68°	38'	75°	15'	81°	42'	46°	1'	44°	26'	43°	6'
C.	68	39	75	14	81	40	46	6	44	29	43	9
Na.	68	41	75	11	81	34	46	32	44	42	43	24
Tl.	68	44	75	8	81	29	47	0	44	57	43	40
F.	68	48	75	3	81	22	47	33	45	15	44	3
			RbMn salt.		CsMn salt.				RbCd salt.	CsCd salt.		
Li.	—		67°	10'	60°	10'	—		72°	20'	68°	4'
C.	—		67	8	60	7	—		72	21	68	2
Na.	—		67	5	59	57	—		72	26	67	53
Tl.	—		67	1	59	46	—		72	31	67	44
F.	—		66	55	59	28	—		72	37	67	28

It will be interesting to follow the variation just referred to with the aid of the curves of Figs. 36 to 40. In the case of the zinc salts (Fig. 36), the more rapid convergence of the *c* curve compared with that of the *a* curve causes a progressive diminution of the relative separation of *b* and *c* compared with *a* and *b*, and therefore an increase in the optic axial angle on passing from the potassium to the rubidium salt; the fact that the *a* curve converges more rapidly as the caesium salt is approached tends to diminish the effect, and so the increase of angle exhibited by the caesium salt is not so large as

was the former increase. The same applies to the iron salts (Fig. 37). In the case of the cobalt group (Fig. 39), the difference between the optic axial angles of the potassium and rubidium salts is almost the same as that between the rubidium and caesium salts, as the c curve also converges more rapidly as the caesium salt is approached. The different chemical nature of copper is again illustrated by the much smaller optic axial angle, due to the fact that the c velocity is at its maximum removal from the b value in each of the copper salts, as shown in Fig. 40, while the a value is exceptionally close to the intermediate value; moreover, the a curve is concave, whereas in all the other groups it is convex.

The nickel group is specially interesting, as exhibiting, in the case of the caesium salt, a reversal of the median lines. It will be observed in the table that the optic axial angle given is over 90° . This of course is the obtuse angle, but it is this angle which is comparable with the others because its median line (the second) is the analogous direction to the directions of the first median lines of the other two salts. The relations of the velocities along the axial directions of the optical ellipsoid which determine this have already been fully stated with reference to Fig. 38, and it only remains to point out that the optic axial angle phenomena are precisely what would be expected from those relations. The following statement concerning it should be included in the general conclusions to be drawn from this investigation.

The first median line is the minimum axis of the optical ellipsoid c in every salt of the series except caesium nickel sulphate, and the sign of double refraction is consequently positive. In the case of caesium nickel sulphate a reversal of the median lines occurs, the first median line being the maximum axis a and the sign of double refraction negative. This is a direct consequence of the operation of the second rule concerning the velocity ratios as explained in the general statement concerning this salt which follows the rule. In accordance with these relationships, the optic axial angle is already unusually large in potassium nickel sulphate, and the operation of the rule of progressive change in the optic axial angle renders it so large when the caesium salt is reached that it exceeds 90° , and the median line which had hitherto been the first becomes the second.

It now remains to discuss the optic axial angle phenomena of the magnesium group of salts. Caesium magnesium sulphate exhibits one of the most interesting cases of crossed axial plane dispersion yet known in connection with monoclinic symmetry. Its extraordinary refraction phenomena have already been fully discussed, and have been shown to be another direct consequence of the operation of the rule concerning the velocity of light vibration. In view of the pre-

vious experience with normal rubidium sulphate, where extremely feeble double refraction was combined with the very near approach to coincidence of two of the velocity values, it appeared most probable that a similar state of matters in the case of cæsium magnesium sulphate would be accompanied, as in the former case, by great sensitiveness of the optic axial angle to change of wave-length of the illuminating light and to change of temperature. The results given in the detailed description of this salt show in how interesting a manner this supposition proves to be correct. The main facts may be briefly summarised in the following terms.

In the case of the three salts containing magnesium the progressive alteration of optic axial angle proceeds according to the rule from the potassium to the rubidium salt. Owing, however, to the remarkable relationships of the velocities along the three axial directions when the cæsium salt is reached, brought about by the operation of the rule previously enunciated and described in the general statement concerning this salt following the enunciation, quite extraordinary optic axial angle phenomena are exhibited by crystals of cæsium magnesium sulphate, including very large dispersion of the optic axes for different wave-lengths of light, a crossing of the optic axial planes, and great sensitiveness to change of temperature. Owing, moreover, to the exceptionally close approximation of the extreme values of the velocity, corresponding to extremely feeble double refraction, section-plates require to be 5 mm. thick in order to afford sharply defined interference figures. For Li light the optic axes are separated about 18° in the symmetry plane. As the illuminating light is changed through yellow towards the blue, the axes approach each other more and more until for blue light of the wave-length 450, they unite in the centre of the field and an apparently uniaxial figure is produced. On still further diminishing the wave-length, the axes again separate, but in the plane at right angles to their former one, and for G light the separation in this plane amounts to about 7° . These values refer to the true angle $2V_a$; the separation for $2E$, the apparent angle in air, is about 26° in the symmetry plane for Li light and 13° in the plane at right angles for G light. On warming the crystal, the axes in the symmetry plane also approach each other, and at 50° the uniaxial cross and circular rings are produced for F light, at 70° for Tl light, at 85° for Na light, at 100° for C light and 103° for Li light, when the dispersion occurs entirely in the plane at right angles to the symmetry plane. If allowed to cool immediately, the section-plate is not injured, and the phenomena recur in the reverse order. The separation of the axes, however, is permanently slightly reduced by the experiment. These beautiful phenomena are the direct result of the operation of the rule connecting the atomic weight of the contained alkali metal with the velocity of light vibration.

In connection with the alteration of the optic axial angle brought about by change of temperature, a further interesting fact has been revealed, connecting the nature of the change with the relative atomic weights of the contained alkali metals. The following tabular statement shows the order and the amounts of change observed in the apparent optic axial angle in air, produced by a rise of 50° of temperature, in the cases of those salts for which such observations were practicable.

Alteration of apparent Angle in Air, $2E$, for 50° .

Second metal contained	Alkali metal contained		
	K.	Rb.	Cs.
Mg.....	Increase of $2\frac{1}{4}^\circ$..	No appreciable alteration	Decrease of exceptional nature
Zn.....	„ $2\frac{1}{4}$..	Increase of $1\frac{1}{4}^\circ$	Decrease of $2\frac{1}{2}^\circ$
Fe.....	„ 2 ..	„ 1	„ $1\frac{1}{2}$
Ni.....	„ $2\frac{1}{2}$..	„ $1\frac{1}{2}$	Angle too large to measure
Co.....	„ $2\frac{1}{4}$..	„ 2	„ „
Cu.....	„ 9 ..	„ $3\frac{3}{4}$	Decrease of $1\frac{1}{2}^\circ$
Mn.....	—	„ 1	„ $2\frac{1}{2}$

It will at once be apparent that

Rise of temperature causes an increase in the optic axial angles of the potassium salts usually amounting to about $2\frac{1}{4}^\circ$ for a rise of 50° ; the effect of a similar change of temperature on the rubidium salts is to provoke a smaller increase of angle, inappreciable in the case of rubidium magnesium sulphate but usually amounting to about $1\frac{1}{2}^\circ$. In the case of the caesium salts, a decrease of optic axial angle is always observed under like circumstances, averaging 2° , but exceptionally large in the case of caesium magnesium sulphate as previously stated. The copper salts again exhibit the individuality of that metal in exhibiting larger increases, of 9° and $3\frac{3}{4}^\circ$ respectively, in the cases of the potassium and rubidium salts of that group. In all cases, however, it is observed that the rubidium salt of any group occupies an intermediate position with an optic axial angle exhibiting but slight change on rise of temperature between the corresponding potassium salt exhibiting a larger positive change and the caesium salt of the same group which exhibits a negative change.

This fact, illustrating the perfection with which change of atomic weight of the alkali metal dominates even minutest details of the optical properties of the crystals, suggests the question as to what are the corresponding changes brought about by rise of temperature in the velocities of light vibration along the three axial directions.

For the reasons stated in the introduction and in connection with the refractive indices of the first salt described (KMg sulphate), the refractive indices could not be so accurately determined at 70° with this series of salts containing water of crystallisation, as to enable full reliance to be placed upon the individual values for the different wave-lengths and for the different axial directions, as indicative of slight changes in dispersion or in the relations of the three indices, the mean lowering of the refraction being all that could be determined with certainty. The changes in optic axial angle, however, indicate that the increase of velocity brought about by rise of temperature is greatest along the ϵ axis and least along the a axis. The more rapid approach of ϵ to b would account for the angle increasing in the potassium and rubidium salts, but, owing to the much closer approximation of the a and b values in the caesium salts, the smaller change along the former axis would be relatively most important in effecting alteration in the relations of the three values, particularly in the case of caesium magnesium sulphate, and hence a decrease of angle would occur. That this is so was clearly proved in the case of the salt just mentioned, for the two images of the slit refracted by the prisms affording the indices α and β were observed, on warming, to approach, coincide, pass each other, and separate on opposite sides, indicating the approach and interchange of the a and b values. It is quite evident that any large change of ϵ short of actual approach to b would be incompetent to prevent the approach to apparent uniaxial properties, both as regards refraction and optic axial angle phenomena. The other groups undoubtedly behave similarly as regards relative changes of velocity, although their cases are not so extreme.

The order of dispersion of the median lines is the same throughout the series with the exception of two salts. These are the caesium magnesium and caesium copper salts, and both are cases in which there is very near approach to coincidence of the α and β refractive indices. The amount of the dispersion is very small, rarely approaching half a degree between Li and F, and usually not more than a quarter of a degree. Hence it is much too small to enable differences between the potassium, rubidium, and caesium salts of any one set to be determined.

One further fact remains to be noticed, concerning the salts containing manganese and cadmium.

Although the potassium salts of the groups containing manganese and cadmium have not yet been prepared, the results afforded by the rubidium and caesium salts containing manganese and cadmium are so similar to those yielded by the other rubidium and caesium salts of the series that there can be no reasonable doubt that, if the potassium salts could be prepared, they would exhibit relationships to the respectively analogous

rubidium and caesium salts similar to those which have been found to exist in the six groups whose members have all been studied.

It may be worth while to indicate the probable morphological and physical constants of these two possible salts of the series, in case they should ever be prepared. Taking into consideration all the facts presented in the foregoing discussion of the results of this investigation, there can be little doubt that the following values will not be very far removed from the truth.

Potassium manganous sulphate, $K_2Mn(SO_4)_2 \cdot 6H_2O$ —

Axial angle β , $75^\circ 13'$.

Ratio of axes, $a : b : c$, $0.739 : 1 : 0.497$.

Relative density, 2.110.

Orientation of axes of optical ellipsoid, $a : c$, 13° .

Refractive indices (Na), α 1.469, β 1.475, γ 1.488.

Optic axial angle, 70° .

Potassium cadmium sulphate, $K_2Cd(SO_4)_2 \cdot 6H_2O$ —

Axial angle β , $75^\circ 20'$.

Ratio of axes, $a : b : c$, $0.737 : 1 : 0.495$.

Relative density, 2.325.

Orientation of axes of optical ellipsoid, $a : c$, 12° .

Refractive indices (Na), α 1.474, β 1.480, γ 1.492.

Optic axial angle, 74° .

SUMMARY OF CONCLUSIONS.

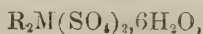
The foregoing communication has been confined exclusively, with the exception of the forecast of the properties of the two hitherto unprepared potassium salts of the series, to the actual observations made during the course of this work, and the results are consequently a collection of facts. Such theoretical considerations and speculations as may be deduced from them, bearing on the interesting question of the constitution of the structural unit, the so-called physical molecule or crystal element, and other problems, will be advanced in a separate communication.

In order that the whole work on this series of salts may be conveniently reviewed at once, the conclusions concerning their morphology, taken, in abridged form, from the previous communication, are included.

The complete series of conclusions now follows, those from the previous memoir being Nos. 1 to 6.

Morphology

1. The salts of the monoclinic series of double sulphates,



containing cæsium as the alkali metal, exhibit the greatest facility of formation and deposition in the form of crystals, and those containing potassium least; the salts containing rubidium occupy an intermediate position in this respect.

2. The characteristic habit of the crystals of the potassium salts of the series is widely different from that exhibited by the crystals of the cæsium salts, and the habit assumed by the crystals of the rubidium salts is intermediate between the two.

3. The morphological obtuse axial angle β increases with increase in the atomic weight of the alkali metal contained, and its magnitude in any rubidium salt of the series is approximately midway between that in the potassium and that in the cæsium salt containing the same second metal. The relative amounts of change brought about in the magnitude of the axial angle by replacing the alkali metal potassium by rubidium, and the latter by cæsium, are thus approximately in direct simple proportion to the relative differences between the atomic weights of the metals interchanged. The changes in the axial angle referred to are of considerable magnitude, usually exceeding a whole degree in each case, and are therefore far removed from the limits of error.

4. The magnitudes of all the angles between the faces of the crystals of the salts of this series containing rubidium as the alkali metal lie between the magnitudes of the corresponding angles upon the crystals of the salts containing potassium and cæsium respectively. The differences between corresponding angles, except in the case of the axial angle, are not generally in simple proportion to the differences between the atomic weights of the alkali metals; the maximum deviation from simple proportionality occurs in the prism zone, where the ratio of the differences, brought about respectively by the replacement of potassium by rubidium and rubidium by cæsium, varies according to the nature of the second metal present from 1 : 2 to 1 : 3. Hence, as the atomic weight becomes higher, it exercises an influence on the angles greater than in mere numerical proportion to its increase.

5. The alkali metals R exert a preponderating influence in determining the geometrical form of the crystals of the salts of this series, the angles being altered on replacing one such metal by the next higher or lower to an extent attaining a maximum of more than a whole degree in certain angles, whilst the replacement of the second metal M by any other of the same family group is unattended by any material change in the morphological angles.

The different chemical nature of copper, compared with the other second metals, is seen in the differences, sometimes amounting to a degree, between the absolute values of the angles of the salts contain-

ing this metal and those of the analogous salts containing the other second metals. The relations presented by the three salts containing copper, however, are in rigorous accordance with rules 3 and 4, a fact indicating that those rules are not merely fortuitous.

6. Although the importance of the morphological axial ratios, as indicative of the change of geometrical form on replacing one alkali metal by another, is greatly diminished by the occurrence of simultaneous mutually neutralising changes in the angles which determine them, it is generally observed that, in any group of three salts containing the same second metal, the ratios for the rubidium salt lie between those of the potassium and caesium salts, and somewhat nearer to those of the potassium salt.

7. The whole of the salts of the series exhibit a common cleavage direction parallel to the orthodome $r'\{\bar{2}01\}$.

Volume.

8. The relative density increases by an approximately constant amount for each of the two specific changes throughout the series, when potassium is replaced by rubidium or the latter by caesium. The difference evoked by the former change is larger than that produced by the latter in the proportion of 5 : 4.

9. An increase in molecular volume occurs when potassium is replaced by rubidium, or the latter metal by caesium. The amount of the increase is approximately constant for each of the two specific changes, the replacement of potassium by rubidium being invariably accompanied by an increase of about 9.3 units, whilst the interchange of caesium for rubidium results in the relatively larger increase of about 13 units.

10. The determination of the molecular volume is pre-eminently a function of the alkali metal R, change of the second metal M being accompanied by a relatively small change of volume. Thus, although the difference between the atomic weights of magnesium and either zinc or copper is nearly the same as that between either potassium and rubidium or rubidium and caesium, yet the maximum amount of alteration produced by interchange amongst the first three is less than one unit, whilst the amounts produced by the interchange of the latter are as stated in rule 9, and when potassium is replaced by caesium the change of volume amounts to no less than 22 units.

11. A comparison of the distance ratios, obtained by combining the morphological axial ratios with the molecular volume, indicates that the replacement of potassium by rubidium, or the latter by caesium, is accompanied by a marked increase in the separation of the centres of the structural units or groups of units along each of the axial directions, corresponding to the increase in volume. The distance

ratios of any rubidium salt of the series are consequently intermediate between those of the potassium and cæsium salts containing the same second metal. The relative amounts of increase when rubidium replaces potassium, on the one hand, and when cæsium replaces rubidium, on the other, are approximately equal along the inclined axis a , but are considerably greater along both the axis of symmetry b , and the vertical axis c , when cæsium replaces rubidium than when the latter replaces potassium. As regards the relative amounts of increase along the directions of the three axes, the extension is invariably much the greatest along the axis of symmetry b , and least along the vertical axis c . Usually the extension in the latter direction does not fall much behind that along the inclined axis; but in the copper salts the individuality of that metal manifests itself in a considerable augmentation of the extension along the inclined axis at the expense of a corresponding decline of extension in the direction of the vertical axis.

Optics.

12. The orientation of the variable axes lying in the symmetry plane of the optical velocity ellipsoid, the polar reciprocal of the optical indicatrix of Fletcher, of every rubidium salt of the series, is intermediate between that for the potassium and that for the cæsium salt containing the same second metal. The maximum axis of the optical ellipsoid a lies nearest to the vertical morphological axis c in the potassium salt of each group, and is furthest removed for the cæsium salt. The intermediate position for the rubidium salt is always considerably nearer to the position for the potassium salt than to that for the cæsium salt, the replacement of rubidium by cæsium being attended by a much greater change of orientation than in mere arithmetical proportion to the change in atomic weight. The optical ellipsoid thus rotates about its intermediate axis b , which is coincident with the morphological symmetry axis b , when one alkali metal is replaced by another. For any potassium salt of the series, it is situated so that its major axis, a , is but slightly inclined to the vertical morphological axis c , in the obtuse axial angle ac ; for the corresponding rubidium salt the inclination is greater, and for the cæsium salt greater still, and to a much larger extent.

The different chemical nature of copper, as compared with the other second metals, is again manifested by the fact that the major axis a , of the optical ellipsoid of potassium copper sulphate, is inclined at so exceptionally large an angle to the vertical axis c as to be in front of the normal to the basal plane, whereas it is behind that normal in the other potassium salts of the series.

13. The refractive indices of any rubidium salt of the series are, without exception, intermediate between those of the potassium and caesium salts containing the same second metal, and nearer to those of the potassium salt. An increase in the atomic weight of the contained alkali metal is accompanied by an increase in the refractive power of the crystal, and the increase in refraction becomes relatively greater as the atomic weight becomes higher. In the case of the intermediate β indices, whose corresponding direction of vibration is the invariable symmetry axis b , the amounts of increase due respectively to the replacement of potassium by rubidium and of rubidium by caesium vary slightly, according to the second metal present, from 1 : 3 to 1 : 4.

14. The relative velocities of light vibration along the three axes of the optical ellipsoid of the crystals of every rubidium salt of the series are intermediate between the velocities along the corresponding axial directions in the crystals of the potassium and caesium salts containing the same second metal. Increase in the atomic weight of the alkali metal is accompanied by an increase of resistance to the vibrations of light waves along each of the axes of the ellipsoid, and this alteration is relatively much greater when caesium replaces rubidium, than when the latter replaces potassium. In the case of the invariable direction of the axis b , the relative amounts are as 3 : 1; the amounts along the axis a are always slightly larger than those along b , and in the same proportion, whilst those along the axis c are in every case much less, and the difference between the effects of the two replacements is more pronounced.

15. An increase in the atomic weight of the alkali metal is accompanied by convergence of the values of the velocity along the three axial directions abc towards unity, and, consequently, by a diminution in the amount of the double refraction. This property is already a very feeble one in the potassium salts, and it is extremely weak in the caesium salts; the rubidium salts occupy an intermediate position in this respect. The amounts of change in the velocity along the two directions of the axes a and b , when potassium is replaced by rubidium, or the latter metal by caesium, being but slightly different, the relations of these two velocities are only slightly changed; the slower rate of change along the c axis, however, has the effect of introducing more considerable changes, in the form of convergence, in the relations between the value for this axis and the other two axial values. Both the former slight relative alteration and the latter more considerable one are progressive in character, the rubidium salt invariably occupying an intermediate position.

16. The preceding rule receives somewhat remarkable confirmation in the case of caesium nickel sulphate. With the exception of this

salt, the whole of the salts of the series exhibit positive double refraction. Owing to the fact that in the potassium nickel salt the a and b values are at their maximum separation for the series, although still nearest together of all the three values in accordance with positive double refraction, the operation of the rule causes it to happen that, in the cæsium salt, the c value, in consequence of its more rapid rate of convergence, has approached nearest the intermediate value b , and so this salt ought to exhibit negative double refraction, a presumption in complete accord with actual observation.

17. Another extraordinary effect of the operation of rule 15 is afforded by the refraction phenomena of cæsium magnesium sulphate. The difference between the a and b values is at its minimum for the potassium salts of the series in the case of potassium magnesium sulphate, and the rule of convergence towards unity results in the ratio $a : b$ actually arriving at unity for the cæsium salt. Owing to the existence of the usual slight difference in dispersion along the axial directions, the coincidence is only absolute for wave-length 450 in the blue. The difference of the two velocities, or of the corresponding refractive indices, is about 0.0001 for sodium light, and 0.0002 for lithium light, the order being as usual throughout the series; for violet G light the values also differ by about 0.0001, but the order is reversed. Hence for wave-length 450 cæsium magnesium sulphate exhibits apparent uniaxial properties. The differences just enumerated for other wave-lengths are so slight that a 60° prism affording these indices exhibits only one image of the spectrometer slit, even for lithium light, unless an eye-piece of very high power is employed in the telescope.

From this and the preceding conclusion 16, it will be evident that although the slight influence of the second metal, which is chiefly observed as regards the ratio $a : b$, cannot be expressed according to any rule involving the atomic weight of that metal, yet its specific nature is of considerable importance in determining the optical phenomena presented by the crystals.

18. The whole of the specific and molecular optical constants, calculated by means of the formulæ of Lorenz or of Gladstone and Dale, for every rubidium salt of the series, are intermediate between those of the potassium and cæsium salts containing the same second metal.

The replacement of potassium by rubidium, and of the latter by cæsium, is accompanied by a diminution of specific refraction and specific dispersion, the amount of which is twice as great when the former chemical change occurs as when the latter substitution is effected. The maximum diminution in specific refraction occurs along the axis c ; the somewhat smaller amounts of diminution along a and

b are almost identical, the amount along **b** being invariably, however, slightly the larger.

The same chemical changes, involving an increase in the atomic weight of the alkali metal, are attended by an increase of molecular refraction and molecular dispersion, the amount of which is greatest when cæsium replaces rubidium, the proportions for the two changes in molecular refraction being as 3 : 5. The amounts of increase of molecular refraction are nearly the same along **a** and **b**, that along the former direction is slightly the greater, and is the maximum increase; the minimum increase occurs along **c**.

These rules are equally valid, whether the constants are calculated by the formulæ of Lorenz, or of Gladstone and Dale, and whatever may be the wave-length for which the comparison of refraction constants is made. Moreover, as refraction and density are similarly affected by change of temperature, they are independent of temperature.

The influence of the second metal in bringing about changes in the molecular optical constants is but slight compared with that due to the alkali metal. It is, however, perceptible in the case of the more intimately related metals magnesium, zinc, and cadmium. The specific refraction diminishes when magnesium is replaced by zinc, and again when zinc is replaced by cadmium, whilst the molecular refraction increases under the same circumstances. The amount of the change is greatest, in the case of the specific refraction, when magnesium is replaced by zinc, and, in the case of the molecular refraction, when zinc is replaced by cadmium, a similar order as regards atomic weight as was observed on replacement of the alkali metal.

19. Excluding the salts containing magnesium, the cæsium salt of which is not strictly comparable with the other two salts, on account of the extraordinary conditions following the operation of rule 15, the optic axial angle (angle between the optic binormals of Fletcher) of any rubidium salt of the series is intermediate between the optic axial angles of the potassium and cæsium salts containing the same second metal, whatever wave-length is chosen for the comparison. This rule is in complete accordance with rule 15, the progressive change there referred to leading to a progressive change in the optic axial angle, which varies in character in the different groups, according to the relative rates of convergence of the extreme values of the velocity towards the intermediate value on replacing the alkali metal by one of higher atomic weight.

This variation in the character of the progressive change in the optic axial angle is due to the influence of the second metal.

20. The first median line is the minimum axis of the optical ellipsoid **c** in every salt of the series, except cæsium nickel sulphate,

in accordance with the positive sign of double refraction. In the cæsium rickel salt, a reversal of the median lines occurs, the first median line being the maximum axis a and the sign of double refraction negative, a direct consequence of rule 15, as described in the statement concerning this salt which follows the rule. In accordance with the velocity relationships there referred to, the optic axial angle is already unusually large in potassium nickel sulphate, and the operation of the rule of progressive change in the optic axial angle renders it so large when the cæsium salt is reached that it exceeds 90° , and the median line, which had hitherto been the first, becomes the second.

21. In the case of the three salts containing magnesium, the progressive alteration of optic axial angle proceeds, according to the rule, from the potassium to the rubidium salt. Owing, however, to the remarkable relationships of the velocities along the three axial directions when the cæsium salt is reached, brought about by the operation of rule 15, and described in paragraph 17, quite extraordinary optic axial angle phenomena are exhibited by the crystals of cæsium magnesium sulphate, including very large dispersion of the optic axes for different wave-lengths in crossed axial planes, and great sensitiveness to change of temperature. Indeed, cæsium magnesium sulphate exhibits one of the most interesting cases of crossed axial plane dispersion yet described in connection with crystals of monoclinic symmetry, and the whole phenomena are the direct result of rule 15, connecting the atomic weight of the contained metal with the velocity of light vibration.

22. Rise of temperature causes an increase in the optic axial angles of the potassium salts of the series, usually amounting to about $2\frac{1}{4}^\circ$ for a rise of 50° ; the effect of a similar change of temperature on the rubidium salts is to provoke a smaller increase of angle, inappreciable in the case of rubidium magnesium sulphate, but usually amounting to about $1\frac{1}{2}^\circ$. In the case of the cæsium salts, a decrease of optical axial angle is always observed under like circumstances, averaging 2° , but exceptionally large in the instance of cæsium magnesium sulphate from the cause just described. The copper salts again manifest the individuality of that metal in exhibiting larger increases than usual of 9° and $3\frac{3}{4}^\circ$ respectively, in the cases of the potassium and rubidium salts of that group. In all cases, however, it is observed that the rubidium salt of any group occupies an intermediate position, with an optic axial angle exhibiting but slight change on rise of temperature, between the corresponding potassium salt exhibiting a larger positive change, and the cæsium salt of the same group, which exhibits a negative change.

23. Although the potassium salts of the groups containing man-

ganese and cadmium have not yet been prepared, the results afforded by the rubidium and cæsium salts containing manganese and cadmium are so similar to those yielded by the other rubidium and cæsium salts of the series, that there can be no reasonable doubt that if the potassium salts could be prepared, they would exhibit relationships to the respectively analogous rubidium and cæsium salts similar to those which have been found to exist in the six groups whose members have all been studied.

24. The foregoing results have clearly demonstrated that the alkali metal R exerts a predominating influence in determining the crystallographical characters of the double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, the influence of the second metal M being comparatively slight. It has been further established that the salts of each group, containing the same second metal, exhibit a regular progression of crystallographical properties corresponding to the progression in the atomic weight of the alkali metal contained. With regard to every property, morphological or physical, the rubidium salt of every group stands intermediate between the potassium and the cæsium salt of that group. It has also been generally observed that the replacement of rubidium by cæsium is accompanied by a much greater modification of the crystallographical characters than the interchange of rubidium for potassium, indicating that change in the atomic weight of the alkali metal becomes more potent in its modifying influence as the atomic weight becomes higher, than in mere arithmetical proportion to that change. Moreover, this statement is rigorously correct as regards even the minutest details of the physical properties, and for all temperatures within whose limits the salts are capable of existing. Further, the extraordinary optical properties exhibited by one member of the series, cæsium magnesium sulphate, have been shown to be the direct result of the operation of this generalisation, and without it would have been inexplicable. So absolutely general, without exception, is it in its application to the 22 salts investigated, that it is now possible to predict in detail the properties which would be exhibited by the two hitherto unprepared salts of the series, potassium manganous sulphate, and potassium cadmium sulphate, if these salts should ever be isolated in the crystallised condition.

That the collection of rules now established is really entitled to be called a generalisation, and is not merely fortuitous, repeated in every group of the series, on account of the similar chemical nature of the second metals and the slight influence which they exert in modifying the properties of the crystals, is conclusively demonstrated by the results of the investigation of the copper group. The different chemical nature of this metal has been unmistakably emphasised, with regard to almost every property, by the exceptional character of

the absolute values of the various morphological and physical constants. Yet the relations of these values for the three salts containing copper are in every instance in rigorous accordance with the rules found for the rest of the series.

The final conclusion of this investigation, therefore, is that

The alkali metal R exerts a predominating influence in determining the characters of the crystals of the isomorphous monoclinic series of double sulphates, $R_2M(SO_4)_2 \cdot 6H_2O$, and the whole of the crystallographical properties of the potassium, rubidium, and cæsium salts containing the same second metal M are, in the case of every such group throughout the series, functions of the atomic weight of the alkali metal which they contain.

XXXV.—*Comparison of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Cæsium, and general Deductions therefrom concerning the Influence of Atomic Weight on Crystal Characters.*

By ALFRED E. TUTTON, Assoc. R.C.S.

It is of considerable importance to compare the results of the detailed investigation of the crystallographical characters of the rhombic normal sulphates of potassium, rubidium, and cæsium, communicated to the Society in 1894 (Trans., 1894, **65**, 628), with those of the memoir preceding this, concerning the monoclinic double sulphates of the isomorphous series $R_2M(SO_4)_2 \cdot 6H_2O$, containing the same three alkali metals. The latter communication has been confined to the actual results of the experimental work. The conclusions of the former memoir are also all related to matters of fact, being the expression of the incontrovertible results of most careful measurements and determinations of physical constants, with the exception of conclusion 10 (p. 713), and more particularly the latter portion of that paragraph, in which certain speculations were indulged in relating to the problem of the nature of the crystal element. The considerations upon which those speculations were based are fully set forth in pp. 661 and 662 of the memoir, and will be discussed subsequently in the next communication, in the light of the results of the investigation of the double sulphates. It is most important in the first place, however, to review side by side the results based upon the experimentally ascertained facts in connection with the two investigations.

It has been shown that *the alkali metal R exerts a predominating*

influence in determining the crystallographical characters of the double sulphates. Hence the relations between the potassium, rubidium, and caesium salts of each group, that is, containing the same second metal, are fairly comparable with the relations exhibited between the simple sulphates of those metals themselves, as evidences of the effect of change in the atomic weight of the alkali metal.

The *habit* assumed by the crystals of rubidium sulphate, or of any rubidium salt of the series of double sulphates, is intermediate in character between the habits exhibited by the corresponding potassium and caesium salts.

The *morphological angles* of the rubidium salt, either simple or double, are invariably intermediate between the corresponding angles of the analogous potassium and caesium salts. Owing to the smallness of the differences in the case of the simple sulphates, no definite statement could be made regarding the relative effect of replacing potassium by rubidium, and the latter by caesium; but in the case of the larger differences presented by the double sulphates, where the symmetry is of a lower order, it was observed that as the atomic weight of the alkali metal becomes higher it exercises a relatively greater effect in modifying the morphological angles. It was interesting to find, however, that in the case of the monoclinic axial angle β , the angle between the two morphological axes lying in the plane of symmetry, the change of angle was approximately in direct simple proportion to the change in atomic weight.

The *morphological axial ratios* of any rubidium salt, simple or double, were also found to lie between those of the corresponding potassium and caesium salts.

The *relative density*, *molecular volume*, and *distance ratios*, that is to say, the whole of the constants connected with the extension in space, are also invariably intermediate in either the simple sulphate of rubidium or any rubidium double salt of the series under discussion, between the corresponding constants for the analogous potassium and caesium salts, and as regards the volume and the distance ratios the replacement of rubidium by caesium is always accompanied by a much larger change than when potassium is replaced by rubidium. It thus appears that extension occurs along each axial direction whenever the atomic weight of the alkali metal is raised, whatever be the nature of the symmetry, and that the amount of the extension is a function of the atomic weight, which involves higher powers of that property than the first.

It is of interest to note that the amount of increase in molecular volume on passing from a potassium to a rubidium salt in the series of double sulphates is practically constant, about 9.3 units, and similarly on passing from any rubidium salt to the corresponding caesium salt, when the larger increase is about 13 units. These

amounts of increase, however, are not quite the same as those corresponding to the replacement of potassium in the simple sulphate by rubidium, and the latter subsequently by cæsium, which were observed to be somewhat less, 8·4 and 11·4. It is, doubtless, of some significance that the replacement of one alkali metal by another should be accompanied by appreciably greater change in volume in the double sulphates than in the simple salts.

It is next important to ascertain whether the alkaline sulphates occupy the same volume in their simple state as in the double sulphates. Fortunately there is excellent data available, as regards the volume of the M metals, in the results of the investigation of Thorpe and Watts (*Trans.*, 1880, **37**, 102) concerning the volumes of the vitriols. In the course of that work they determined the relative densities of the anhydrous sulphates of magnesium, zinc, ferrous iron, manganese, nickel, cobalt, and copper, and the density of anhydrous nickel sulphate in the state of good crystals was also determined by Lepierre and Lachaud (*Compt. rend.*, 1892, **115**, 115), and by Klobb (*Compt. rend.*, 1892, **114**, 836). There is no data available for cadmium sulphate. Thorpe and Watts also determined the volume of the water of crystallisation in magnesium sulphate in various stages of hydration. They showed that the firmly held seventh molecule of water, the water of constitution, occupied the volume 10·7, whilst the various molecules of water of crystallisation occupied somewhat increasing volumes as their number present in the salt increased, ranging from 13·3 to 16·2, and averaging about 15. If then we take the volume of 6H₂O as six times 15, or 90, and add to this the volume of the anhydrous M sulphate, and the volume of the alkaline sulphate determined by the author, we should, if the alkali sulphate occupied the same volume when crystallised alone as when present in the double salt, obtain a number practically identical with the observed molecular volume of the double salt. The following calculations will show how far this is the case.

The relative density of anhydrous magnesium sulphate is 2·709. Its molecular volume is therefore 44·3, and the volume of MgSO₄·6H₂O = 44·3 + 90 = 134·3.

	Observed.
Mol. vol. of KMg sulphate = 65·3 + 134·3 = 199·6.	198·2
„ RbMg „ = 73·8 + 134·3 = 208·1.	207·6
„ CsMg „ = 85·2 + 134·3 = 219·5.	220·7

The relative density of ZnSO₄ is 3·623, the volume 44·4, 0·1 higher than MgSO₄. Hence

	Observed.
Mol. vol. of KZn sulphate is 199·7.	197·7
„ RbZn „ 208·2.	207·2
„ CsZn „ 219·6.	219·9

The relative density of FeSO_4 is 3.346, the volume 45.4, 1.1 higher than MgSO_4 .

		Observed.
Mol. vol. of KFe sulphate is	200.7.	200.1
„ RbFe „	209.2.	209.2
„ CsFe „	220.6.	222.6

The relative density of MnSO_4 is 3.282, the volume 46.0, or 1.7 higher than MgSO_4 .

Mol. vol. of KMn sulphate would be 201.3. Not observed.

		Observed.
„ RbMn „ is	209.8.	213.7
„ CsMn „ „	221.2.	226.6

The relative density of NiSO_4 in crystals is 3.67, the volume 42.2, or 2.1 less than MgSO_4 .

		Observed.
Mol. vol. of KNi sulphate is	197.5.	195.6
„ RbNi „	206.0.	204.9
„ CsNi „	217.4.	217.9

The relative density of CoSO_4 in 3.472, the volume 44.8, or 0.5 greater than MgSO_4 .

		Observed.
Mol. vol. of KCo sulphate is	200.1.	197.8
„ RbCo „	208.6.	207.3
„ CsCo „	220.1.	220.3

The relative density of CuSO_4 is 3.606, the volume 44.1, or 0.2 less than MgSO_4 .

		Observed.
Mol. vol. of KCu sulphate is	199.4.	198.3
„ RbCu „	207.9.	207.6
„ CsCu „	219.3.	220.2

Hence it is evident that *within very narrow limits the volume of the alkali sulphate is the same in the double salt as it is in the simple salt itself*. As regards these narrow limits, it will be noted that the differences between the calculated values of the potassium and caesium salts containing the same second metal is invariably 20, whilst the observed difference was 22. This, of course, is because the former smaller difference was observed between the simple sulphates of potassium and caesium, whose values are used in the calculations. There is absolutely no doubt as to the accuracy of the densities of the simple alkaline sulphates, and the results for all the several series of double salts confirm each other. The further consideration, however, of this minute difference in the amount of change of volume, accompanying replacement of one alkali metal by another, in the simple sulphates and the double salts respectively, may with advan-

tage be deferred until the completion of the work on the analogous selenates. For the present purpose, it is sufficient to observe that the volume occupied by the alkaline sulphate in the double salt is practically identical with its volume in the free state.

Another point of importance, indicated by the agreement of the observed values with those calculated from the data specified, is that none of the molecules of water are present in the double salts in the condition of water of constitution occupying the smaller volume 10·7.

It is especially interesting to point out that the molecular volumes of the simple alkaline sulphates are very considerably less than the sum of the atomic volumes, even less than the atomic volume of the alkali metal alone. The atomic volume of potassium is 45·5, of rubidium 56·3, and of cæsium 70·7, and 2 atoms would correspond to volumes of 91, 112·6, and 141·4 respectively, whilst the molecular volume of K_2SO_4 is only 65·3, of Rb_2SO_4 73·8, and of Cs_2SO_4 only 85·2. Hence an enormous contraction must follow the combination of the atoms of the alkali metal with the acid radicle.

In the case of the rhombic simple sulphates, the three principal optical directions, the optical elasticity axes according to the older theory, the principal axes of the *optical indicatrix* of Fletcher, and of its polar reciprocal, the optical velocity ellipsoid referred to throughout the preceding communication, are, in accordance with the nature of the symmetry, identical with the directions of the morphological axes. Consequently they suffer no change of direction when one alkali metal is replaced by another, the symmetry remaining unaltered. On the other hand, only one of these axes remains constant in direction in the double sulphates, the one which is coincident with the morphological symmetry axis, and normal to the symmetry plane. The other two principal rectangular axes of the optical ellipsoid are only subject to the conditions that they must lie in the symmetry plane, and preserve their rectangularity, being free to move together in the symmetry plane. It has been shown that the optical ellipsoid actually rotates round the fixed symmetry axis as the atomic weight of the alkali metal is raised, and that the replacement of rubidium by cæsium is accompanied by a much greater amount of rotation than when potassium is replaced by rubidium. The amount of this rotation is very considerable, reaching a maximum in the magnesium salts of 33° between the potassium and the cæsium salts. It is one of the most interesting and doubtless significant results derived from the investigation. The rotation follows in direction the movement of the inclined morphological axis, assuming the vertical axis to remain vertical; for as the atomic weight of the alkali metal increases the obtuse angle between the inclined and vertical axes widens, by about 2° between potassium and cæsium, and the two rectangular axes of the optical ellipsoid lying in the symmetry plane move round in the

same direction as the inclined morphological axis, but to a much larger extent. It would, therefore, appear that the alteration of the morphological axial angle is connected with the alteration in the orientation of the optical ellipsoid, that is to say, the alteration in the angle between lines of contiguous structural units, parallel to the two directions of the vertical and inclined morphological axes, is intimately connected with the relatively very large alteration in the directions of maximum and minimum velocity of light vibration through the crystal which is observed.

The *refractive indices* of the simple normal sulphate of rubidium, or of any rubidium salt of the series of double sulphates, are intermediate between the indices of the analogous salts containing respectively potassium and caesium, and invariably lie nearer to those of the potassium salt. It was observed, both as regards the simple sulphates and the double sulphates, that an increase in the atomic weight of the alkali metal is accompanied by an increase in the refractive power of the crystals, and that, in accordance with the latter portion of the previous statement, the increase in refraction becomes relatively greater as the atomic weight becomes higher. It is of importance to observe, however, that the actual differences between the refractive indices of corresponding potassium, rubidium, and caesium salts are much larger in the case of the simple sulphates than in any group of the double sulphates. Thus, the intermediate β indices for sodium light for the three simple sulphates are: for K_2SO_4 1.4947, for Rb_2SO_4 1.5133, and for Cs_2SO_4 1.5644, a difference between K and Cs of 0.0697, whilst for the magnesium group, which exhibits the greatest difference of any group of the double sulphates, the β_{Na} indices are: potassium magnesium sulphate 1.4629, rubidium magnesium sulphate 1.4689, and caesium magnesium sulphate 1.4858, exhibiting a difference of 0.0229, or only one-third the difference observed for the simple sulphates. This is doubtless due to the greater magnitude and complexity of the double sulphate molecule, a change in the atomic weight of even the most important element present, the alkali metal, being naturally incapable of modifying the physical properties to so large an extent as would be the case in a simple molecule such as that of the normal sulphate.

The *velocity ratios* (for light), or ratios of the refraction reciprocals, the optical elasticity ratios of the older theory, naturally follow similar laws to the refractive indices; in both simple and double sulphates the ratios for a rubidium salt are intermediate between those for the corresponding potassium and caesium salts. Increase in the atomic weight of the alkali metal is accompanied by an increase of resistance to the vibrations of light waves along each axis of the optical ellipsoid, and the resistance interposed is much greater when caesium replaces rubidium than when the latter replaces potassium,

that is to say, it becomes greatly augmented as the atomic weight rises, far more so than in proportion to the augmentation in atomic weight.

The progressive changes in the velocity ratios introduced by increasing the atomic weight of the alkali metal, graphically represented by the changes in the lengths of the axes of the optical ellipsoid, are such in both simple and double sulphates as to result in a convergence of the maximum and minimum values of these ratios towards unity. That is, as the atomic weight of the alkali metal rises the differentiation in optical behaviour in different directions in the crystals becomes less marked. In all the groups of double sulphates, except the magnesium group, the operation of this rule results in the *double refraction*, already weak in the potassium salts, becoming feebler in the rubidium salt, and feebler still in the cæsium salt. In the magnesium group it results in identity of two of the three values being actually attained when the cæsium salt is reached, and hence the remarkable optical phenomena presented by cæsium magnesium sulphate described in the preceding communication. In the simple sulphates the result is even more extraordinary, for the convergence of the two extreme values is so rapid that they are almost arrived at unity in the rubidium salt, and actually so if the temperature is slightly raised, thus causing normal rubidium sulphate to exhibit similar remarkable optical phenomena to cæsium magnesium sulphate; just beyond the rubidium salt the curves representing these same two values coincide at the ordinary temperature and cross each other, afterwards diverging until, when the cæsium salt is reached, they are further apart than they were in the potassium salt, but the sign of double refraction is completely reversed.

Hence the results as regards both the simple sulphates and the double sulphates are in perfect agreement in regard to the regularly progressive nature of the changes introduced into the optical ellipsoid by increase of the atomic weight of the alkali metal. It is doubtless significant that the striking effect, in the case of the simple sulphates, of the rule regulating these changes is most nearly reproduced in the magnesium group of the double sulphates, in which the atomic weight of the second metal magnesium is much lower than that of any other of the second metals, and hence the total relative weight of the molecule is least, and the magnesium salts are therefore more largely affected by change of the alkali metal.

The whole of the *specific and molecular optical constants* of rubidium sulphate, and of every rubidium salt of the series of double sulphates, have been shown to be intermediate between the analogous salts containing respectively potassium and cæsium. Both with respect to the simple sulphates and to the double sulphates it was observed that increase in the atomic weight of the alkali metal is accompanied by

a diminution of specific refraction and dispersion, the amount of which is much greater when potassium is replaced by rubidium than when the latter metal is replaced by cæsium. The same changes are productive of an increase in the molecular refraction and dispersion, and the amount is much the greatest when cæsium replaces rubidium, the opposite of the case for the specific constants. These rules were further shown to be independent of the nature of the light and of temperature.

The molecular refraction data now available for the simple sulphates and so large a number of double sulphates afford some interesting and not unimportant comparisons.

It was found that when rubidium replaced potassium in potassium sulphate a mean difference of molecular refraction for the ray C of 5.48 Gladstone and Dale or 3.11 Lorenz units was observed. In the double sulphates the like chemical change was found to be accompanied by a mean increase varying in the different groups from 5.11 to 5.32 or 2.97 to 3.09 according to the formula employed. The replacement of rubidium in rubidium sulphate by cæsium was accompanied by a mean increase of 10 Gladstone and Dale units or 5.43 Lorenz units; in the double sulphates a similar replacement corresponded to a mean increase of 9.26 to 9.96 or 5.19 to 5.50 such units. It is evident, therefore, that approximately identical changes in molecular refraction accompany similar chemical changes both in the simple salts and in the double salts. The mean values from all the results, both for the simple and double sulphates, are 5.27 and 9.72 Gladstone and Dale units for the replacement respectively of potassium by rubidium, and the latter by cæsium, or 3.05 and 5.41 Lorenz units.

Now, the molecular refraction equivalent of potassium has been determined with very great care by Gladstone, after taking account of recent determinations of other workers besides himself, and he ascribes the value 7.85 to it (*Trans.*, 1891, **59**, 597). Assuming this number to be correct, and adding to twice this value, 15.7, corresponding to the 2 atoms of potassium, the increment of 5.27 on replacing potassium by rubidium, we obtain, assuming no extraordinary changes occur, the value 20.97 for 2 atoms of rubidium and 10.5 as the refraction equivalent of rubidium. Adding the further increment of 9.72, for the replacement of rubidium by cæsium, to 20.97 we obtain 30.69 for the value of 2 atoms of cæsium, or 15.35 for the refraction equivalent of cæsium.

The values for rubidium and cæsium previously given by Gladstone (*Phil. Trans.*, **159**, 13: *Proc. Roy. Soc.*, **18**, 49) are 12.1 and 19.1 respectively, and by Kanonnikoff 12.04 and 19.55 (*J. pr. Chem.*, 1885, **31**, 321, 497).

It is evident that either these latter values of the two metals are incorrect, or that some extraordinary diminution of molecular refraction occurs in both simple and double sulphates.

A most valuable confirmation of the author's values for the molecular refraction of the simple sulphates has recently been published by Gladstone (*Trans.*, 1895, **67**, 840), who has determined the refractive indices in solution. The numbers thus obtained for the refraction equivalents are: for K_2SO_4 32.15, practically the same as the 1891 value, for Rb_2SO_4 38.39, and for Cs_2SO_4 47.57. The mean values corresponding to the three crystal indices obtained by the author for the three respective salts were 32.30, 37.79, and 47.77. Hence it is clear that solution merely gets rid of the differential refraction in different directions, the value for the dissolved salt being practically identical with the mean of the three values along the principal optical directions of the crystal. Gladstone has also determined the molecular refraction of potassium zinc sulphate, and obtained the number 95.94, a value almost absolutely identical with the author's mean value for the crystal 95.90.

Before proceeding further it will afford some guide if the values of the radicle SO_4 are deduced from the refraction equivalents of the simple sulphates, assuming 7.85, 10.5, and 15.35 to be the equivalents of potassium, rubidium, and cæsium respectively. Deducting twice these values, for the 2 atoms of each respective alkali metal, from the above quoted mean values for crystals of K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 , the numbers 16.6, 16.79, and 17.07 are obtained for SO_4 . Now, even the highest of these is appreciably lower than the value previously found by Gladstone for this radicle, 17.5 (*Trans.*, 1891, **59**, 597), and if the previously accepted values of Gladstone and of Kanonnikoff for rubidium and cæsium were adopted the numbers for SO_4 derived from the two corresponding salts would be much lower still, namely, 13.59 and 9.57, numbers which are absurdly low. Hence one of two things occurs. Either the refraction equivalents hitherto accepted for rubidium and cæsium are incorrect, at any rate in these salts, or, being correct, there is some disturbing cause in operation which results in a considerable absorption of refractive energy, and which becomes more powerful as the atomic weight of the alkali metal rises. For it is evident that if the molecular refractions of K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 are calculated, assuming Gladstone's 1891 values for SO_4 and potassium, and the older values of Gladstone and of Kanonnikoff for rubidium and cæsium, the number obtained for K_2SO_4 will be practically identical (33.2) with that derived from actual observation, while the numbers for Rb_2SO_4 (41.7) and Cs_2SO_4 (55.7) will be considerably larger than those calculated from the observed refraction, the latter number exhibiting the greatest discrepancy.

It is also possible to calculate with especial accuracy the molecular refraction of two of the groups of double sulphates, those containing magnesium and zinc; for Gladstone has recently determined the values of MgSO_4 and of ZnSO_4 (Trans., 1895, **67**, 838), and in the same memoir publishes the results of a most careful re-determination of the value for water. Assuming these values, $\text{MgSO}_4 = 24.1$, $\text{ZnSO}_4 = 26.32$, $\text{H}_2\text{O} = 6.01$, and taking first the author's determined values for K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 , and afterwards the values calculated for these salts, on the assumption that $\text{K} = 7.85$, $\text{Rb} = 12.1$, and $\text{Cs} = 19.1$, the following results are obtained.

Salt.	Mean values derived from direct observation.	Value calculated on first assumption.	Value calculated on second assumption.
$\text{K}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	92.41	92.46	93.36
$\text{Rb}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	97.73	97.95	101.86
$\text{Cs}_2\text{Mg}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	107.42	107.93	115.86
$\text{K}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	95.90	94.68	95.58
$\text{Rb}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	101.22	100.17	104.08
$\text{Cs}_2\text{Zn}(\text{SO}_4)_2, 6\text{H}_2\text{O} \dots$	110.75	110.15	118.08

It is evident that the numbers calculated on the first assumption agree very closely with the values derived from the actual measurements, while those based upon the second assumption are much too high for the rubidium and caesium salts, and particularly the latter. The first series of numbers for the zinc salts agree still more closely if Kanonnikoff's value for Zn (9.8) be taken, along with Gladstone's recent value for SO_4 , when ZnSO_4 becomes 27.3, one unit more than Gladstone's value for ZnSO_4 .

Hence the same fact is as clearly demonstrated in the double sulphates as in the simple sulphates, that either the hitherto accepted values for Rb and Cs are too high, and the latter to the greatest extent, or there is some internal source of loss of refractive energy which is more effective as the atomic weight of the alkali metal rises. Which of the two possibilities is correct had perhaps better be left undiscussed until further observations on other compounds of these metals are available. Doubtless the investigation of the selenates and double selenates on which the author is now engaged will afford additional information on this point.

The refraction equivalents of the remaining double salts of the series, derived from direct observation, will now be compared with the values calculated by use of the author's observed values for K_2SO_4 , Rb_2SO_4 , and Cs_2SO_4 , and Gladstone's older values for ferrous Fe (12), Ni (10.4), Co (10.8), Cu (11.6), Mn (12.2), Cd (13.6), and his more recent values for SO_4 (17.5), and H_2O (6.01), in order to ascertain

whether a similar agreement occurs to that shown between the values in the first two columns in the preceding table for the magnesium and zinc salts.

Salt.	Mean value derived from direct observation.	Calculated value.
$K_2Fe(SO_4)_2 \cdot 6H_2O$	96·92	97·86
$Rb_2Fe(SO_4)_2 \cdot 6H_2O$	102·03	103·35
$Cs_2Fe(SO_4)_2 \cdot 6H_2O$	112·00	113·33
$K_2Ni(SO_4)_2 \cdot 6H_2O$	96·33	96·26
$Rb_2Ni(SO_4)_2 \cdot 6H_2O$	101·50	101·75
$Cs_2Ni(SO_4)_2 \cdot 6H_2O$	111·25	111·73
$K_2Co(SO_4)_2 \cdot 6H_2O$	96·63	96·66
$Rb_2Co(SO_4)_2 \cdot 6H_2O$	101·91	102·15
$Cs_2Co(SO_4)_2 \cdot 6H_2O$	111·76	112·13
$K_2Cu(SO_4)_2 \cdot 6H_2O$	97·29	97·46
$Rb_2Cu(SO_4)_2 \cdot 6H_2O$	102·54	102·95
$Cs_2Cu(SO_4)_2 \cdot 6H_2O$	111·80	112·93
$Rb_2Mn(SO_4)_2 \cdot 6H_2O$	102·95	103·55
$Cs_2Mn(SO_4)_2 \cdot 6H_2O$	112·49	113·53
$Rb_2Cd(SO_4)_2 \cdot 6H_2O$	105·80	104·95
$Cs_2Cd(SO_4)_2 \cdot 6H_2O$	114·58	114·93

It will be observed that the agreement is fairly close throughout. If, however, instead of the observed values of Rb_2SO_4 and Cs_2SO_4 , corresponding to the values for Rb and Cs of 10·5 and 15·35 respectively, being used in the calculations, the usually accepted values for Rb and Cs, 12·1 and 19·1 are employed, the calculated values for the rubidium double salts will be 3—4 units higher than the observed values, and for the caesium double salts 7—8 units higher, as in the cases of the magnesium and zinc salts.

It is, therefore, undoubtedly a fact that the same refraction equivalents which were observed in the case of the simple sulphates apply also to those salts when combined with the sulphates of magnesium, zinc, iron, nickel, cobalt, copper, manganese, and cadmium to form the double sulphates crystallising with 6 mols. of water.

It is interesting to note that the greater difference which is observed in molecular refraction between the caesium and rubidium salts than between the potassium and rubidium salts, whether simple or double, is entirely in accordance with the relations of the difference between the atomic refractions of the alkali metals themselves. If the author's values, as derived from the sulphates and

double sulphates, are taken, the differences between the refraction equivalents of potassium and rubidium and caesium and rubidium respectively are 2.7 and 4.8. If Gladstone's values are taken, the differences are 4.3 and 7.0 respectively. In either case the ratio is of the same order as in the salts.

The optic axial angle phenomena of both simple and double sulphates were shown to be precisely in accordance with the requirements of the rule regarding the progressive change in the velocity ratios or the relationships of the axes of the optical ellipsoid. With regard to the double sulphates, in every group except that containing magnesium, where extraordinary relationships of those ratios are exhibited in the case of caesium magnesium sulphate, the optic axial angle of any rubidium salt is intermediate between that of the potassium and that of the caesium salt of the same group. In the case of the magnesium group the remarkable crossed axial plane dispersion of the optic axes of the caesium salt, and the great sensitiveness of the optic axial angle to change of temperature, were shown to be the direct effect of the operation of the rule of convergence of the velocity ratios towards unity, which resulted in two of the axial values of the optical ellipsoid actually attaining unity, but at any one temperature only for a particular wave-length, hence the crossing of the optic axial plane and the simulation for that particular wave-length of uniaxial optical properties. In the simple sulphates the result of the operation of the same rule regarding the convergence of the maximum and minimum axes of the optical ellipsoid towards equality has been shown to lead to an even more extreme result, namely, that unity is almost attained at the ordinary temperature in the case of the rubidium salt, and actually so on slightly raising the temperature, causing the optic axial angle of that salt to be likewise extremely sensitive to change of wave-length and of temperature, and to exhibit the phenomenon of crossed axial plane dispersion at temperatures slightly elevated above the ordinary; further, that in caesium sulphate those axial values are again separated, but in the contrary direction, as would be expected after the meeting if the change were continuous; and hence this salt exhibits negative double refraction, and the plane of the optic axes is perpendicular to that in the potassium salt. The whole of these complicated and very beautiful, as well as unusual, phenomena are thus immediately explained on the assumption of progressive changes corresponding to the progressive change in the atomic weight of the alkali metal.

It has now been conclusively shown that *the whole of the morphological and physical characters of the crystals of the rhombic normal sulphates of potassium, rubidium, and caesium, and of any group of the*

monoclinic double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which those simple salts of the three alkali metals are combined with the sulphate of either magnesium, zinc, iron, manganese, nickel, cobalt, copper, or cadmium, whilst conforming to the same symmetry and exhibiting the general similarities proper to isomorphous series, present well-defined differences which are functions of the atomic weight of the alkali metal which those salts contain, and usually functions which involve higher powers of the atomic weight than the first.

The completion of the work on the potassium, rubidium, and caesium salts of sulphuric acid, therefore, establishes beyond doubt, as regards these three definitely related metals and this particular acid, that *The characters of the crystals of isomorphous series of salts are functions of the atomic weight, that is to say of the energy of which atomic weight is the expression, of the interchangeable dominant elements belonging to the same family group of the periodic system which give rise to the series.* There is strong presumptive evidence that this will eventually prove to be a general law of Nature. The investigation of the analogous selenates and double selenates which the author is now undertaking, will afford a substantial addition to the information already accumulated.

XXXVI.—*The bearing of the Results of the Investigations of the Simple and Double Sulphates containing Potassium, Rubidium, and Caesium on the Nature of the Structural Unit.*

By ALFRED E. TUTTON, Assoc. R.C.S.

THE ultimate structure of organised solid matter, to which we assign the term crystalline, is undoubtedly one of homogeneity, and to the variations in the type of homogeneity are due the variations in crystalline form which such solid matter presents. The truth of this important statement can no longer be seriously disputed, in view of the comparatively complete state to which our knowledge regarding the possible homogeneous partitioning of space has now been brought by the labours of Barlow, following upon those of Sohncke, Schönflies, and Federow, and the fact that the possible types of homogeneous structures correspond precisely with the observed varieties of crystalline symmetry. In its most recent form, as stated to the Mineralogical Society on November 19, 1895, Barlow's definition of a homogeneous structure is substantially as follows. A homogeneous structure is one to every point in which there correspond other precisely similar points which are uniformly distributed in space, and round every point in such a system the arrangement of the remainder

is the same as round every other; the whole rigid structure may consist of an arrangement of material of any nature, the only conditions being that it shall be constant in form and uniformly repeated throughout its whole extent. Barlow especially insisted in his latest communication referred to that, if the structure is divided into space units, it is not necessary that such space units which compose the homogeneous structure should individually have the symmetry of the homogeneous structure itself; it is only necessary that any point taken upon, within, or about it should be represented by precisely similar corresponding points upon every other unit of material which makes up the homogeneous structure.

The question next arises: What is this unit of material or space unit? Is it the chemical molecule of the substance which by its uniform repetition builds up the crystal of the particular chemical compound, and some point upon, within, or about which may be considered as a Sohnckian point as now defined by Barlow, or is it a unit of greater complexity than the chemical molecule? The evidence at the present time available regarding the nature of the crystal element will first be briefly reviewed, and afterwards reinforced by the teaching of the investigation of the simple sulphates of potassium, rubidium, and cesium, and of the double sulphates of the series $R_2M(SO_4)_2 \cdot 6H_2O$, in which R is represented by the same three metals of the alkalies.

The main evidence, which is usually regarded as favouring the assumption that the molecular condition of a substance in the solid state is more complex than in the liquid and gaseous states, is that afforded by polymorphism. It is assumed that the fact that many substances are capable of existing in different types of homogeneous structures, differing greatly in symmetry, is due to the different nature of the units of which these structures are composed, that is, to different states of polymerisation of the chemical molecule. The thermal changes which invariably accompany the conversion of any one such form into any other favours this view, inasmuch as it closely resembles the display of thermal activity which accompanies purely chemical changes. Moreover, whenever rise of temperature occurs on the conversion of one modification into another, the relative density is found to increase, as, for instance, when the best known monoclinic form of sulphur changes into the more stable and denser rhombic form. One of the most striking and instructive cases is that of ammonium nitrate described by Lehmann. This salt melts at about 168° , and when the liquid is allowed to cool crystals belonging to the cubic system, and therefore isotropic, commence to separate; when the temperature has fallen to 127° , doubly refracting rhombohedral crystals form, and at 87° rhombic crystals develop,

and are deposited in regular order about the rhombohedra. Hence it would appear that these different forms of ammonium nitrate are due to a difference in the state of aggregation, probably a difference in the molecular complexity of the crystal element. In all probability the liquid consists of chemical molecules corresponding to the simple empirical formula, the first solid form may also consist of molecules of like simplicity whose freedom of rolling motion is now arrested, or it may consist of double molecules, and each further form may be due to the addition of a further simple chemical molecule to the structural unit. Anyhow, each successive crystalline form produced during the cooling of the liquid is denser than the previous one. In the case of sulphur, it is the form of least symmetry, the monoclinic, which is first produced on cooling of the liquefied substance, the higher rhombic being the denser and more stable form into which the monoclinic crystals become eventually transformed with loss of heat. So that it is not the general rule that the higher type of symmetry is first assumed on cooling from a state of liquefaction, and consequently the degree of symmetry of a homogeneous crystal structure does not depend entirely on the simplicity of structure of the crystal element if the above explanation is correct.

In explanation of these facts concerning polymorphism or physical isomerism, two alternative assumptions are open to us. The first is that each different form corresponds to a crystal element containing a specific number of chemical molecules, or, possibly, if two or more of the forms belong to the same system of symmetry, as is frequently the case, to a different arrangement of the chemical molecules within the crystal element. The second is that the same simple molecular state exists throughout, the crystal element consisting of the chemical molecule, and that the different types of homogeneous structures owe their origin to contiguous molecules being separated at different distances, with all the attendant consequences as regards the forces, attributable either to the various atoms composing the molecule or to the molecule as a whole, which determine the nature of the symmetry of the homogeneous structure. It is quite conceivable that a rigid structure should be produced at a temperature but slightly below the melting point, and stable for this temperature, which would prove unstable and tend to collapse at a lower temperature, naturally with evolution of heat. The first assumption, however, appears to be supported by the preponderating weight of evidence, and is quite in accordance with the facts concerning numerous well investigated cases of—so-called—physical isomerism among the carbon compounds. An admirable *résumé* of the large amount of data now available is given by Arzruni in his *Physikalische Chemie der Krystalle*.

The acceptance of isomerism, whether it be called chemical or physical, of a crystal element comprised of different numbers of simple chemical molecules for the various polymorphic forms of substances which exhibit such, does not, however, necessarily involve the assumption that the crystal element of any and every substance is invariably composed of more than one chemical molecule. It is true that the most stable form of several polymorphic substances is the one to which the greatest molecular complexity would naturally be assigned, such, for instance, as the rhombic forms of sulphur and ammonium nitrate. Yet it is still possible that in all cases where no polymorphism has been observed, the crystal element may be the chemical molecule itself. Particularly is this likely to be the case with complicated molecules consisting of a large number of atoms. Hence each case must be investigated on its merits. Even if the numbers of chemical molecules comprising the crystal elements of the various forms of certain polymorphic substances were established with certainty, and it were proved that the stable varieties consisted of crystal elements built up of several chemical molecules, it would not follow that other substances should be built up of crystal elements of similar complexity, although there would be some ground for assuming this, in a more or less modified form. Moreover, the considerable display of thermal activity manifested during the polymerisation of the simple chemical molecules to form polymorphic varieties indicates that these varieties are more in the nature of different chemical substances, just as oxygen and ozone are ordinarily considered to be, than mere physically different varieties of the same substance, and that the whole structural molecule of each is in reality a complex chemical molecule. The constitution of these structural molecules of the various varieties could probably be immediately deduced from their thermal relationships provided the number of simple chemical molecules present in any one variety were ascertained with certainty. The question of the constitution of the crystal element of any substance, or of any variety of a polymorphic substance, will therefore have to be approached from other standpoints, and the most certain way of accumulating relevant evidence regarding it is by carrying out detailed investigations of the morphological and physical relationships of the crystals of the definitely related members of isomorphous series, in order that first the particular type of homogeneous structure common to the series may be discovered, and that subsequently the forces requisite to produce such an arrangement, and the orientated modifications which are observed as the consequence of the specific replacement of one atom for another in the chemical molecule, may lead to definite knowledge regarding the nature of the crystal element itself. Most weighty

evidence, which must also be taken into account, are the now fully ascertained conditions of homogeneous symmetry as laid down by Barlow, the data regarding the range of molecular forces, and the bearing of the now rapidly developing theory due to van't Hoff which regards isomorphous mixtures as solid solutions.

It will be convenient to consider the evidence from the three latter sources before discussing the results of the investigations of the simple and double sulphates containing potassium, rubidium, and caesium. Barlow's conditions of homogeneous symmetry have already been referred to; it is only necessary to bear particularly in mind that these conditions do not require that the space unit shall be endowed with the same symmetry as the structure itself.

In a lecture to the Society (Trans., 1888, 53, 222), Prof. Rücker presented a complete summary of then available trustworthy data, including that contributed by himself and Reinold, concerning the range of molecular forces. The most interesting conclusions from the point of view of the subject under discussion are as follows: The smallest appreciable thickness of a silver film, as estimated by Wiener, is 0.2 of a millionth of a millimetre; the mean distance between the centres of nearest liquid molecules is 0.07—0.02 of a millionth of a millimetre, and the inferior limit to the diameter of a gaseous molecule is 0.02 of a millionth of a millimetre, the two last estimates being due to Lord Kelvin. Now, it is quite evident, assuming the size of a solid molecule, or, at any rate, the distances apart from centre to centre of solid molecules, to be not very materially different to the estimate given for liquid molecules, an assumption undoubtedly warranted by the usual relatively slight difference in volume on passing from the liquid to the solid condition, that the thinnest attainable film of silver cannot possibly contain more than ten silver molecules in its thickness, and probably not more than five or six. Hence if the solid structural unit of silver is even composed of simple chemical molecules consisting of two atoms each, there cannot be more than this quantity of such units present in the thickness in question, and if it should happen that in this thickness there is only one structural unit, which is scarcely likely, then the structural unit of silver cannot possibly contain more than ten, and probably not more than five or six, chemical molecules, and there would be less still if more than one structural unit is present in the film. The problem is thus restricted within these limits.

Brillouin (*Ann. Chim. Phys.*, 1895, 540) discusses the limits of the domain of molecular action in connection with the superficial tensions of crystalline forms. He shows first that the existence of crystalline faces is dependent on the fact that the domain of molecular action extends to more than one molecular distance, and deduces from the law of

rational indices of the principal crystalline faces the conclusion that the limits of the domain extend to only a small number of molecular distances, probably not more than four or five. He then shows that in crystals the domain of repulsion of a molecule is very small, that the limiting surface of the zone of repulsion is a neutral zone, and that beyond this attraction is apparent for a few molecular distances. He further shows that orientation of the molecular forces is produced owing to the fact that the atomic magnitudes are sensible fractions of the molecular distances, and the distribution of the atoms in the molecule consequently exercises considerable influence. He finally concludes that the molecule exercises no appreciable action beyond eight or ten molecular distances, but that the action is sensible up to four or five such distances, and further, that the faces exert appreciable superficial tensions, which vary from the cause stated in different directions in the crystal.

The conclusions to be derived from existing data as to the range of molecular forces are thus of considerable importance, whether they are taken as applying to the chemical molecules, or, if these are not identical with the crystal elements, to the structural units composed of two or more chemical molecules. The main point which they indicate is that the crystal element, if not identical with the chemical molecule, is not likely to contain more than four or five chemical molecules, and most probably less.

The bearing of recent applications of the theory of van't Hoff, which regards crystallised mixtures of isomorphous salts as solid solutions of one in the other, must now be referred to. The application of the theory to the determination of the nature of the crystal element is fully discussed in two recent communications by Fock (*Ber.*, 1895, **28**, 2734, and *Zeits. für Kryst.*, 1895, **25**, 566). If c_1 and c_2 represents the degrees of concentration of two isomorphous salts in the same liquid solution, or, in other words, the number of molecules in unit volume, and x_1 and x_2 the corresponding degrees of concentration, or the molecular percentages, in the separated mixed crystals, then the theory requires that c_1/x_1 and c_2/x_2 shall be constant, provided the molecular complexity is the same in both the solid and liquid conditions. If the molecule in the solid state is n times as large as in the liquid state, then $\frac{c_1}{\sqrt[n]{x_1}}$ and $\frac{c_2}{\sqrt[n]{x_2}}$ shall be constant. The

dissociation of the salts in the aqueous solution, however, proves to be a disturbing factor, rendering the method more difficult in application than is at first apparent; but this can be largely eliminated by choice of salts in which the solubility is very nearly the same. The mixed crystals formed by one pair of such salts, monopotassium phosphate, KH_2AsO_4 , and the corresponding arsenate, KH_2AsO_4 ,

have been investigated by Muthmann, and the results have been recalculated by Fock from this point of view. The interesting result is disclosed that for both salts c/x exhibits but relatively slight deviation from constancy, whilst c/\sqrt{x} varies much more considerably. Hence Fock concludes that the crystal element in the case of these two salts is the chemical molecule. A similar calculation for potassium permanganate and perchlorate, likewise investigated as regards their mixed crystals by Fock, leads to the conclusion that their crystal elements are composed of two chemical molecules, assuming the latter to be represented by the formulæ KMnO_4 and KClO_4 , or one chemical molecule if the view adopted by many chemists is correct, that the constitutions are $\text{K}_2\text{Mn}_2\text{O}_8$ and $\text{K}_2\text{Cl}_2\text{O}_8$. In the case of these two salts, however, the results are not quite so convincing, as their solubilities are very different, and dissociation consequently enters largely into the problem.

The normal sulphates of potassium, rubidium, and cæsium are very unsuitable for an investigation of this kind, on account of their very great difference of solubility. Whilst potassium sulphate is one of the least soluble of salts, cæsium sulphate is extremely soluble, requiring very little more than half its volume of water, and the rubidium salt is intermediate in solubility.

In his second communication, that to the *Zeits. für Kryst.*, Fock proceeds to show that the above results indicate that in general the symmetry of the crystal element is of a lower order than that of the crystal. If the molecules KH_2PO_4 and KH_2AsO_4 are the crystal elements, no distribution in space of the various atoms in these crystal elements can possibly be endowed with the high symmetry of the tetragonal system which the crystals present. It might be possible, however, with some slight straining of current ideas of atomic linking, to arrange the constituents of the crystal elements, $\text{K}_2\text{Mn}_2\text{O}_8$ and $\text{K}_2\text{Cl}_2\text{O}_8$, in such a manner as to agree with rhombic symmetry. The results derived from the theory of solid solutions would thus appear to be in harmony with the conclusion of Barlow, that the structural unit is not in general endowed with the same high degree of symmetry as the structure itself.

Lengthy reference was made in the communication concerning the normal sulphates of potassium, rubidium, and cæsium (*loc. cit.*, p. 657), to the important memoir which had a short time previously been published in the *Zeits. für Kryst.* (22, 497), by Muthmann, concerning the morphological characters of the phosphates and arsenates of potassium and ammonium, and the permanganates of potassium, rubidium, cæsium, and ammonium. From the changes which occurred in the distance ratios (topic axes) along the three axial directions when one chemical constituent was replaced by another of the

same family group, Muthmann concluded that, provided the crystal element were endowed with like symmetry to the crystal itself, the crystal elements of the isomorphous series of mono-phosphates and arsenates must each consist of eight chemical molecules, and those of the alkali permanganates of four chemical molecules. It was pointed out in the memoir on the alkali sulphates, that if Muthmann's assumption were correct, the nature of the changes in the distance ratios indicated that a similar conclusion, that the crystal element consists of four chemical molecules, must be drawn regarding the sulphates of potassium, rubidium, and cæsium as was deduced from similar changes in the distance ratios of the permanganates of those metals. The whole argument, however, depends on the assumption of a crystal element itself exhibiting the symmetry of the whole structure. It was pointed out that it was difficult to understand why localised change should occur unless the metallic atoms were arranged in closest proximity to the axial directions which exhibited most change on replacing one metal by another. No definite conclusion was, however, ventured on, as the author preferred to await the results of the investigation of the double sulphates.

One point was clearly demonstrated in that memoir, and that was that the type of homogeneous structure prevalent in the simple alkali sulphates was that of the rectangular rhombic prism, the evidence upon which this was based being the cleavage directions, the positions of the planes in which the similar points were most densely packed, and the nature of the forms most largely developed upon the crystals, all of which considerations pointed to the same conclusion.

The nature of the evidence afforded by the investigation of the monoclinic double sulphates will now be discussed. It has caused the author to conceive a totally different idea as to the nature of the crystal element and crystallisation in general to that which a study of the simple sulphates alone would have led, and one which is distinguished by its simplicity, and which is in complete harmony with Barlow's geometrical conception of a homogeneous structure, with the known facts concerning the range of molecular forces, and with Fock's deductions from the theory of solid solutions.

There is a largely preponderating weight of evidence that the point system of the series of monoclinic double sulphates crystallising with six molecules of water is that of the monoclinic primary prism, and not the pinacoidal monoclinic prism corresponding to the pinacoidal rhombic prism which was clearly shown, with no reasonable room for doubt, to be the type of homogeneous structure prevailing in the case of the simple sulphates of potassium, rubidium, and cæsium. The evidence upon which this assumption is based is of a kindred kind to that advanced in support of the conclusion concerning the

latter salts. The two pinacoids are rarely developed upon the crystals of any of the double sulphates of the series to any important extent, and in by far the majority of well-developed crystals are either absent altogether or exist as mere lines. The faces of the primary prism, on the other hand, are always largely developed, and in a vastly preponderating number of cases they are the predominating faces, and frequently the only prismatic (including pinacoidal) form developed. Of the terminal forms, undoubtedly the basal plane exhibits predominance, and is more likely to be the terminal plane of the structure than the orthodome $r'\{201\}$, for in very numerous cases the latter has been absent altogether. In the case of many of the salts, particularly those in which the alkali metal is potassium, a very large proportion of crystals were actually found which on first inspection appeared to exhibit no other faces than those of the primary prism and basal plane; examination with a lens usually revealed minute faces of the clinodome $\{011\}$, and possibly of the orthodome $r'\{201\}$, but in a notable number of instances failed to reveal traces of any such minute faces. It is true, however, that in a few cases, rubidium cadmium sulphate in particular, a preponderating development of the orthodome $r'\{201\}$ was observed, but these were exceptional. Hence the evidence of the relative development of the various forms indicates that the type of structure is that of the primary prism $\{110\}$ and the basal plane $\{001\}$.

The evidence of the cleavage is not so weighty in the monoclinic system as in the rhombic, for there is no restriction to its direction other than that it is either identical with or symmetrical to the plane of symmetry, and if at right angles to the latter there is no restriction as regards its azimuth. It has been shown that the cleavage is perpendicular to the symmetry plane, and that throughout the series it is parallel to the orthodome $r'\{201\}$. This might be taken as evidence in favour of the latter form supplying the terminal planes of points, but against this is the more weighty fact that the area of such a terminal plane would be much greater than if it were the basal plane $\{001\}$, for considerations regarding the capillarity constants prove that faces are much more readily formed along those planes in which the similar points are most densely packed, and therefore in which the area of the parallelogram formed by four adjacent points is least. Assuming the primary prism to form the sides of the parallelogram, the relative area of a terminal plane parallel to the basal plane would be $a \times \frac{b}{2}$. Taking rubidium zinc sulphate as an example, where $a:b:c = 0.7373:1:0.5011$, we have $0.7373 \times \frac{1}{2} = 0.3686$ as the area in question. If the form $\{201\}$ furnished the termination, the area would be $x \times \frac{b}{2}$, where x is the third side of a

triangle of which the two other sides are $2c$ and a , and the angle between them the axial angle β . Calculation for the same salt, for which $\beta = 74^\circ 7'$, gives for x the relative length 1.5988. Hence the area required is one-half this number, 0.7994, a much larger value than that corresponding to the basal plane.

The evidence of the cleavage is chiefly important here in indicating that the type of structure is not that of the pinacoidal prism, for if it were, a cleavage parallel to the symmetry plane would be expected, whereas the cleavage is perpendicular to the symmetry plane, and in a direction not that of the orthopinacoid. If the termination were $r'\{201\}$ the type would be that of an unusually steeply inclined monoclinic prism, whereas a termination parallel $\{001\}$ is very much less so, and far more probable. Of course it is quite possible that $r'\{201\}$ should form the termination in spite of this, but even if so the type would be the same, only much more oblique.

Moreover, the point system would be precisely the same, for r' is a face with simple indices, and therefore the type of structure would provide a plane of points corresponding to it, just as it does with regard to the basal plane.

The area test may also be applied to assist in deciding the question as to whether the pinacoid or the primary prism furnishes the sides of the structure. According to the relations of the lengths of the axes a , b , and c , one of the pinacoids or the primary prism will possess the least area, and the points in the plane containing it will be densest, and therefore most probably the principal point-plane of the series. The area of the clinopinacoid in the case of the typical salt chosen, rubidium zinc sulphate, is $ac \sin \beta = 0.7373 \times 0.5011 \times \sin 74^\circ 7' = 0.3554$. The area of the orthopinacoid is $bc = 0.5011$. The area of the primary prism is $c \times \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2} \times \sin \theta$, where θ is the angle between the edges pp and cp , and is the angle at p in the triangle acp of the spherical projection (p. 343 of the memoir concerning the morphology), and is found by calculation to be $80^\circ 39'$; using this value of θ , the area in question works out to be 0.3071. Hence the plane formed by parallelograms of least area is that corresponding to the primary prism. In the case of the monoclinic double sulphates, it is thus seen that all the various considerations of use for indicating the nature of the homogeneous structure agree in pointing to the type corresponding to the primary prism $p\{110\}$ terminated by the basal plane $c\{001\}$. The axes a and b are thus parallel to the diagonals of the basal plane termination of the prism. The particular type thus indicated corresponds to type 64a of Barlow.

It was shown in the case of the simple sulphates that the type was that of the rectangular (pinacoidal) rhombic prism terminated by the

basal plane, the three axes being thus parallel to the various edges of the prism. The author takes this opportunity of correcting an error which was inadvertently made in calculating the area of the primary prism of those salts (p. 661 of the memoir concerning the simple sulphates). Instead of $\sqrt{a^2 + b^2} \times c$, it should have been

$$\sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2} \times c.$$

Of course the line (trace of the primary prism) joining the ends of the axes a and b , and forming the hypotenuse of the triangle of which the semi-axes are the side and base, can never be greater than both these axes; the problem is to find which is least, one of the axes, the trace of a pinacoid, or the trace of the primary prism. The result is 0.58, intermediate between the brachypinacoid 0.42 and the macropinacoid 0.74. The least area is therefore possessed by one of the pinacoids, and so the rectangular type of structure is probably correct. The error, due to calculating for the diagonal of the rectangular base instead of for the parallel line of half the length joining the ends of the axes, does not affect the conclusion arrived at in the slightest, but it is desirable to correct it. It is most interesting to observe that in the zone of the macropinacoid (plane of greatest area) and the basal plane no intermediate faces were ever observed developed, confirming the validity of the rule that planes of least area are those parallel to which faces are formed with the greatest facility, and *vice versa*.

It should be quite clearly understood that these conclusions regarding the point systems of the two series of salts imply absolutely nothing as regards the shape or nature of the crystal elements. The points only represent the centres of contiguous molecules.

Having thus decided that the results of the two investigations indicate that the types of homogeneous structure prevailing in the two series are those above specified, we now proceed to enquire what further information is to be gained from the investigations relating to the nature of the space units of which these homogeneous structures are composed. The double sulphates will be considered first, as the information their investigation has afforded has thrown new light on the constitution of the simple sulphates.

The distance ratios of the double sulphates were found to increase along each axial direction when potassium was replaced by rubidium and the latter in turn by cæsium, and most considerably along the direction of the symmetry axis b , the extensions along the a and c axes being usually nearly the same, the former being only slightly the greater. In the case of the three copper salts, the peculiar nature of the atom of copper is manifested in an augmenta-

tion of the expansion along the inclined axis a at the expense of that along the vertical axis c . Now no hemihedrism has been observed, the crystals all exhibiting the characters of the prismatic (monoclinic-holohedral) class of the monoclinic system, according to the Sohnckian classification adopted by Groth in the new edition of his *Physikalische Krystallographie*. Further, the minimum number of atoms of the alkali metal possibly present in the crystal unit is two, corresponding to one formula molecule, $R_2M(SO_4)_2 \cdot 6H_2O$. Hence, it must be concluded that the large extension normal to the symmetry plane observed when one alkali metal is replaced by another of greater atomic weight, is due to the fact that the two atoms of the alkali metal are, if in a state of rest, symmetrically arranged with regard to the symmetry plane, or if in a state of restricted motion, the spaces within which the motions are confined are symmetrical to the symmetry plane, that is, their positions of rest or centres of motion must be arranged along the normal to the plane of symmetry.

The complexity of the formula molecule is already so great, consisting as it does of no less than eight simple chemical molecules, one molecule of the alkaline sulphate, one of the M sulphate, and six molecules of water, that, having regard to the established range of molecular forces, if it is necessary to assume the existence of a single crystal element, then this must be represented by not more than one formula molecule. It cannot be conceded that the molecular complexity is greater than this, whether the union of the parts be considered chemical or physical.

We next enquire: Is it necessary to assume the existence of a crystal element embodying the whole formula, or even consisting of two constituents, the anhydrous double salt molecule and the $6H_2O$, in accordance with the suggestion made long ago by Sohncke—in fact, is it necessary to assume the existence at all of a structural unit of any different constitution to the simple chemical molecules themselves? The comparison of the results of the investigations of the simple and double sulphates instituted in the preceding communication affords weighty evidence to the contrary. It was shown that the alkali sulphates occupy in the double sulphates substantially the same volume as they do in the simple salts themselves, whilst, on the other hand, when the various chemical atoms combine to produce the chemical molecule of the alkaline sulphate, a relatively enormous contraction of volume occurs, so much so that the volume of the resulting compound is actually less than the original volume of the atoms of the alkali metal alone, and it cannot be assumed that the negative radicle occupies no volume at all (or less than none, which is absurd). Hence a chemical union of the 2 mols. of the simple

salts is altogether out of the question, for such a union would be accompanied by a change of volume, similar in kind though perhaps less in extent to that which accompanies the formation of a simple salt from its constituent elements, and such change of volume is not observed. Any other union must be of a very loose nature indeed. Moreover, the double salt is only known in the crystallised condition.

Hence the author is impelled to the only reasonable conclusion that in the production of the crystals of the double salts of this series, and hence, probably, of isomorphous series in general, no other structural units are concerned than the chemical molecules of the simple constituent chemical compounds, the alkali sulphate, the M sulphate, and water, and that the fact of their invariable occurrence in the observed molecular proportions is entirely a condition of the type of homogeneous structure in which they find equilibrium. This type has been shown to be, in all probability, that of the primary monoclinic prism with rhombic base, most likely type 64*a* of Barlow. The existence of chemical molecules, and the generalisation of Barlow concerning the homogeneous partitioning of space, is thus all that is necessary in order to account for crystal structure, and for the constancy of molecular proportions in double salts and salts crystallising with water, the assumption of the formation of molecular compounds or complex crystal elements being entirely superfluous.

This conclusion, based upon the volume relationships, offers an explanation of the fact observed by Lehmann, that orientated forces are not essential to the production of crystal structure, that the pedetic or "Brownian" motion of small particles is ample to account for their eventually arranging themselves in the most convenient manner, that is, in a manner resulting in equilibrium. Indeed, anything, such as capillarity or convection current disturbances, that assists the chemical molecules to take up more readily this condition of equilibrium, corresponding to the production of a homogeneous structure, will assist crystallisation. An excellent example is the disturbance of a supersaturated solution, which usually causes instantaneous crystallisation.

With regard to the question as to how the constituent chemical molecules are arranged with respect to each other in the structure, it has been shown from the consideration of the variations in the distance ratios that the two atoms of the alkali metal of each molecule of the alkali sulphate must be symmetrically arranged with respect to the symmetry plane. Also, the fact of the predominance of the alkali metal in determining the character of the crystals indicates that the one atom of the M metal occupies a more central, and therefore less effective, position than the two atoms of the alkali metal. The water molecules may be distributed in any positions about the

molecules of the two simple sulphates, consistent with the many possibilities conformable to type 64a, which latter is also fully competent to account for an arrangement of the simple sulphates in accordance with the two requirements just laid down in conformity with the observed facts. Before proceeding further in this direction, however, it will be advisable to await the further information which the investigation of the selenates cannot fail to afford.

Returning now to the simple alkaline sulphates; in the light of the important conclusions drawn from the investigation of the double sulphates, it is no longer necessary to assume that the crystal element is anything more complicated than the chemical molecule R_2SO_4 . It so happens that in this particular case the molecule can possibly be regarded as endowed with the same rhombic symmetry as the

crystal, for the formula can be represented thus, $R-O-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-O-R$. But

this is only an accident of the constitution of the particular chemical molecule. Such a simple crystal element would be quite capable of accounting for the observed facts of the variations in the distance ratios. Two directions exhibited large change, and one pre-eminently. This latter would undoubtedly correspond to the direction of the line joining the two R atoms, and the other direction of slightly less change, in all probability that perpendicular to this line, and not passing through the doubly-linked (whatever that may mean) oxygen atoms, the effect in the third direction being much lessened by the latter. Whatever may be the actual relative positions of the atoms in space, and whether they are in motion or at rest, the variations of the distance ratios can be readily accounted for by the constitution of the molecule and the well ascertained predominating influence which the alkali metal exerts.

It is instructive to note that the system of the simple sulphates is of higher symmetry than that of the double sulphates, indicating that, in general, the more heterogeneous the composition of a crystal-lised substance the lower is its type of symmetry.

It will be evident, however, that if the crystal element is the chemical molecule, the symmetry of the crystal element need not, and in general will not, possess the same degree of symmetry as the crystal. Its symmetry may be greater than, equal to, or less than that of the crystal, and will, of course, depend on the specific nature and constitution of the particular chemical compound concerned. This conclusion is in complete harmony with that of Barlow derived from the geometrical conception of the homogeneous partitioning of space, and that of Fock deduced from the application of van't Hoff's theory of solid solutions.

The simple conclusion that the formation of double salts of constant composition, and of simple or double salts crystallising with definite amounts of the solvent, in this case water, is entirely due to their finding a condition of equilibrium in a particular type of homogeneous structure, has the inestimable advantage of dispensing with all necessity for the assumption of "linking" between the molecular parts, an assumption which frequently necessitates considerable outrages on the ascertained facts regarding valency.

The assumption that it is the type of structure which determines the molecular composition, and, consequently, in the case of salts containing water of crystallisation, the number of such molecules, there being no linking between the molecular parts, will fully account for the looseness with which the water is frequently held. It has been shown that the stability is at a minimum in the case of the double sulphates in question, when the atomic weight of the alkali metal in the alkaline sulphate is low (and correspondingly, also, the volume of the latter) and the volume of the M sulphate high. The last condition is most extreme in the case of the cadmium salts, with regard to which it was observed that the cæsium cadmium salt exhibited considerable facility of efflorescence, rubidium cadmium sulphate much greater instability, complete efflorescence occurring in a few minutes after removal from the mother liquor, whilst potassium cadmium sulphate, where the alkali metal is lightest, refuses to crystallise with more than 2 mols. of water, and the crystals consequently exhibit another type of homogeneous structure altogether. Similarly, potassium manganous sulphate refuses to crystallise with more than 4 mols. of water, and the crystals again exhibit another type of structure, manganous sulphate having also exceptionally large volume, although not so extreme as in the case of cadmium sulphate. On the other hand, the nickel salts exhibit abnormally small volume, doubtless due to the small volume of nickel sulphate, and potassium nickel sulphate is consequently distinguished as one of the most beautiful salts of the series, perfectly transparent permanent crystals being obtained with the greatest facility.

The conclusion that the crystal element of the simple alkaline sulphates is identical with the chemical molecule is quite in conformity with the fact that the molecular refraction, as determined in solution in water by Gladstone, is identical with the mean of the three values of the molecular refraction afforded by the crystal as determined by the author. It is, therefore, evident that the mean refraction is due to the chemical molecule, and that the differentiation in the directions of the axes of the optical ellipsoid is due to the homogeneous structure. Thus there is no intermediate state, no aggregation of a certain number of chemical molecules to form a crystal element to

account for. Moreover, the alkali sulphate in the crystals of the double sulphate was proved to exhibit there precisely the same molecular refraction as it exhibits in the crystals of the simple sulphate itself, which, to say the least, is quite compatible with the assumption that the same molecular state exists in both.

There remains one interesting optical property to account for, namely, the rotation of the optical ellipsoid of the double sulphates round the symmetry axis as the atomic weight of the alkali metal is changed. In a memoir read at the Ipswich meeting of the British Association in 1895, Barlow accounted for the observed relationships between the morphological and optical symmetry of crystals. From the known influence of the presence of molecular matter on the velocity of light, and the directional optical properties of crystals, it was concluded that ether movements which take place in different directions in the same crystal experience different degrees of resistance and retardation, so that a state of things prevails roughly comparable to what would happen if a space occupied by a crowd of people were studded with posts arranged on parallel lines and evenly distributed; the movements of the crowd as it surged to and fro would be less impeded in some directions than in others, especially if the posts were not round, but of similar section same ways orientated. What are compared in each case are the collective resistances in each direction, and Barlow shows that if the influence of a homogeneous molecular structure on light depends on the arrangement of the molecular matter, it is an average effect, the velocity of a ray in any given direction depending not merely on the resistance to ether movement in some single direction definitely related to the direction of polarisation of the ray, but on that experienced in all other inclined directions in addition, within some wide limits of angular inclination. Eventually he deduces the fact that the velocity figure must be an ellipsoid, the smoothing out, or averaging of, the corrugated surface whose radii would express the relative facility of ether movement in different directions in the crystal naturally leading to such a conclusion. The relative positions of the three axes of the ellipsoid would depend on the nature of the crystal structure. These directions will not necessarily be directions of maximum or minimum facility of ether movement, and, moreover, they will not be ascertainable from the morphological constants unless the degrees of resistance presented in different directions are known, except in the cases of the more symmetrical systems where the positions of these axes are fixed by considerations of symmetry.

The investigation of the monoclinic double sulphates affords most interesting proof that Barlow's conception is correct. In accordance with the conclusion that the chemical molecules retain their inde-

pendence in the structure of the crystal, the type of that structure alone determining the molecular proportions (assuming, of course, that the proportions of the two salts present in the solution from which the crystals separate are such as are observed to be convenient for the production of this particular type of structure, in the case in question equal molecular proportions), each molecule will be able to exert its own effect on the optical properties. Now it has been shown all through the investigation that the alkali metal is of special importance in determining the characters of the crystals, and it was only to be expected, therefore, that the replacement of potassium by rubidium, and of the latter by caesium in the double salts, would exert a pronounced effect in modifying the character of the optical ellipsoid. It has been shown that two atoms of the alkali metal must be symmetrically arranged with respect to the symmetry plane, and that the M metal is in all probability more central, being most likely situated in the symmetry plane; now, if the 2 mols. of the anhydrous sulphate remain—as we conclude they do—independent, it is most unlikely that the alkali sulphate molecule, and the two atoms of the alkali metal which it contains, can be symmetrical to the centre of the whole system, and, therefore, change of the alkali metal would be likely to deflect the direction of greatest facility of ether movement, or, in other words, would produce a rotation of the optical ellipsoid. That this is the explanation is supported by the fact that the rotation is much greater when caesium replaces rubidium than when the latter replaces potassium, for the change of volume was shown to be correspondingly much greater, and, therefore, the retardation, and consequent rotation of the path of greatest facility of light vibration, would be commensurably greater.

It is of interest to note that in the potassium and rubidium salts the direction of one of the axes of the ellipsoid is very nearly that of one of the directions of greatest facility of ether vibration, namely, that between the lines of points (the posts of Barlow's graphic illustration) parallel to the inclined morphological axis *a*. The axis of the ellipsoid in question is usually deflected a few degrees on one side of this path between the points in the case of the potassium salt—it is frequently almost identical with it in the case of the rubidium salt—and is invariably deflected by a considerably greater number of degrees to the other side of the path in the case of the caesium salt; in all cases the position for the rubidium salt is an intermediate one, and nearer to that for the potassium salt.

Moreover, in final confirmation, it has been shown in the previous communication that the direction of the rotation of the ellipsoid, when one alkali metal is replaced by another, is identical with that of the same inclined morphological axis, *a*, and consequently with that of

the lines of similar points parallel thereto and with the path of greatest facility of ether vibration between them.

Thus it will be observed that the simple conclusion to which these investigations has led is capable of explaining the whole of the phenomena described in the preceding communications.

The main points may be briefly summarised in the following terms.

1. The absence of any material contraction in volume when the alkali sulphate enters into the double sulphate, as contrasted with the relatively enormous contraction which occurs when the various atoms combine to form the chemical molecule of the alkali sulphate, together with the facts that the double salt is only known in the solid crystallised condition, and that many of the individual members of the series are eminently unstable, render it highly improbable that there is chemical union between the molecular constituents of the double salts, and indicate that there is no necessity to assume linkage of any kind, but merely aggregation in accordance with such a particular type of homogeneous structure as ensures that they are always present in the same proportion.

2. In the production of crystals it is not necessary to suppose that any other structural units are concerned than the chemical molecules of the chemical compound in question, or of the constituent chemical compounds in the cases of double salts or salts containing water of crystallisation, and the observed fact of the constancy of molecular proportions of the two latter is entirely accounted for by the nature of the type of homogeneous structure in which they find equilibrium.

3. The pedetic or "Brownian" motion of small particles, capillarity, convection currents, or any other slightly agitating forces which assist the chemical molecules to take up this condition of equilibrium necessary for the production of a homogeneous structure, will assist crystallisation. The molecular forces whose domain of action has been shown not to extend beyond a very few molecular distances, need only be concerned in maintaining the general cohesion.

4. Considering the chemical molecule as the structural unit, in general such unit will not be endowed with the same symmetry as the crystal; it may have higher, equal, or lower symmetry according to the specific constitution of the molecule. This is in complete accordance with the generalisation of Barlow concerning the homogeneous partitioning of space, and the conclusion of Fock derived from the theory of solid solutions.

5. These conclusions are in entire accordance with the observed variations of the distance ratios (topic axes) of the two series of salts, and with the refraction phenomena. The distance ratios represent the relative distances apart of the centres of contiguous structural units, the chemical molecules, in the case of the simple sulphates;

and of contiguous groups of structural units, each such group corresponding to the molecular chemical formula, in the case of the double sulphates.

6. The fact that the mean of the three values of the refraction along the axes of the optical ellipsoid afforded by the biaxial crystals of each of the simple alkaline sulphates is identical with the refraction value of that salt as determined by Gladstone in solution, indicates that the matter in a crystal has for refraction purposes the same average effect as the same matter uncrystallised; so that if small cubes were cut at random from a crystal so as to obtain all sorts of orientations, and fitted together, the result would be an isotropic substance having the same refraction as when dissolved in water. This is in most perfect conformity with the supposition that the mean refraction of the crystal is due to the chemical molecule, the orientated differentiation being due to the homogeneous structure.

7. The more heterogeneous the constitution of a crystallised substance the lower in general is its type of symmetry; *e.g.*, the simple alkali sulphates crystallise in accordance with rhombic symmetry, and the double sulphates with 6 mols. of water only in accordance with monoclinic symmetry.

8. The nature of the predominating crystalline faces, as being the planes in the homogeneous structure most closely studded with similar "points," together with the directions of cleavage, agree in indicating that the type of homogeneous structure of the simple alkali sulphates is that of the rectangular pinacoidal rhombic prism, and that of the double sulphates the primary monoclinic prism, probably type 64*a* of Barlow. The term elementary parallelepiped is discarded as being a geometrical fiction which is not required.

9. The phenomenon of the rotation of the optical ellipsoid of the double sulphates, when the atomic weight of the alkali metal is changed, is completely accounted for by the assumption of the above simple constitution for the double sulphates, together with the suggestion of Barlow that the orientation of the optical ellipsoid is the resultant of a process of averaging of the directional retardations, experienced by light waves in traversing the homogeneous structure, due to the arrangement of the molecular matter. The greater amount of rotation when cæsium replaces rubidium, than when rubidium replaces potassium, is thus the direct result of the correspondingly greater increase of volume, largely in a particular direction, which is observed.

XXXVII.—*An Auxiliary Assay Balance.*

By ROBERT LAW.

THE following communication has for its object the description of a new form of balance, which has been designed to meet a want often felt by the writer when weighing the cornets obtained when pursuing the ordinary routine of gold bullion assay.

When weighing these cornets (especially when the gold being assayed varies much in fineness), it becomes very tedious having continually to shift the weights perhaps three or four times for each cornet, it has often occurred to me that a rough balance might be constructed to give accurately the percentage of gold present, and thus make it possible to place the correct weight in the pan, the remaining fractions being found by the rider only.

Let it be understood that this balance to which I allude is an auxiliary balance, so to speak, and in no way affects the final readings of the ordinary assay balance, its object being merely to give the percentage with the previously stated advantage.

It is obvious, therefore, that each cornet will have to be handled twice, placing it first on the rough balance, and then removing it to the ordinary assay scales. It may seem that this double shifting of the cornet would lead to more loss of time than weighing in the ordinary way, and at first this may be so, but after a little practice quite the opposite has been found to be the case, and much of the concentrated attention which makes the assayer's work so monotonous is removed.

The advantages claimed for the balance are

1. It lessens the time of weighing.
2. It saves the assay balance.
3. It reduces the wear and tear on the weights (a factor not to be overlooked, and one which only those who have made or corrected small weights can fully appreciate).

For fully two years balances of this kind have been and are in daily use at the Royal Mint, Melbourne.

The adjoining sketch will make clear the principle of this simple addition to the assayer's tools far better than pages of descriptive matter.

The balance consists of a disc of aluminium, D, 0·3 inch in diameter (Fig. 1) and 0·1 inch thick, into which an arm, A, 1 inch long and 0·05 inch thick, is screwed, the arm being provided with steel bearings N, to support the pan P. The pan itself is 0·75 inch in diameter. R is a steel rod, 0·02 inch in diameter, on which an

adjustable brass ball, B, is screwed. This is to counterpoise the arm A, with pan, &c. The pointer X, which is 4 inches long, indicates the weight, on the scale S, the weight on it being marked from actual trial with the ordinary assay weight. The scale can be set in a ver-

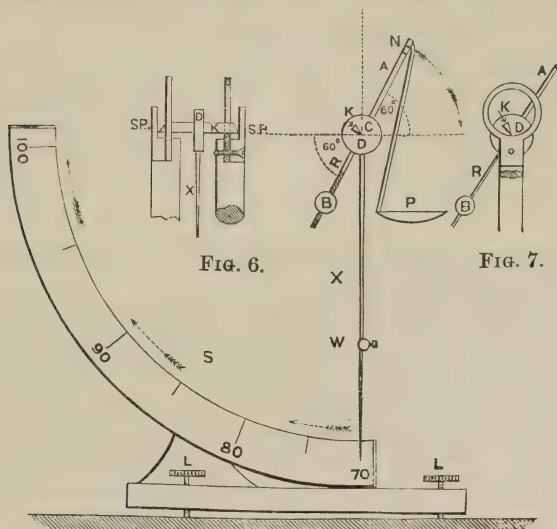


FIG. 1.

- | | |
|-----------------------|-------------------------------|
| A. Arm. | X. Pointer. |
| D. Disc of Aluminium. | W. Adjusting weight. |
| R. Steel Rod. | N. Steel bearing for the Pan. |
| B. Brass Ball. | L. Levelling Screws. |
| P. Pan. | S. Scale. |
| K. Knife edge. | |

tical plane to read from the front, or, better, placed so as to read from the back, this being the position when in use. The whole moves in a vertical plane about the centre C, where is placed the knife edge K. The stand needs little description. It consists of a brass or iron plate, 2 inches by 2 inches by 0.25 inch thick, into which are screwed two pillars which support the planes. It is furnished with levels and levelling screws as illustrated. It is therefore small enough to go into the balance case and stand beside the pan of the ordinary assay balance, which position is found to be the most convenient for use.

The only trouble found was providing a suitable bearing. It was recognised that a knife edge or planes were the most trustworthy, but on account of the great sweep of 90° it was thought impossible to utilise this, so other forms were experimented with. The first trial was with the form illustrated below (Fig. 2).

It consisted of a steel spindle, S, pointed at both ends, working

loosely in hard steel cups, the whole being highly burnished. The results were unsatisfactory. The ultimate intention was to have the spindle and cups of agate, but the results were so discouraging that the whole was rejected in favour of the following modification. The spindle was made as thin as a needle at the ends, and worked on a knife edge practically as shown (Fig. 3).

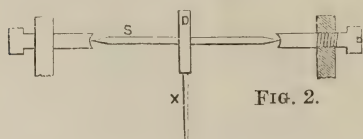


FIG. 2.

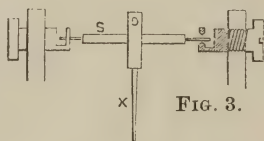


FIG. 3.

The results were more encouraging, but still not sufficiently accurate for the purpose intended.

Before describing the last improvement, I might mention an alteration suggested by the balance mechanician, Mr. Otto, to whom I am much indebted for the way in which he carried out my instructions with regard to the various trials. He substituted a hair spring for the spindle, the spring being stretched tightly between the two pillars of the stand. This gave admirable results at first, in fact so good that this form was adopted in preference to the one with a knife edge, but it had its drawbacks. The spring is affected by variations in the temperature and pressure of the atmosphere, and I suppose

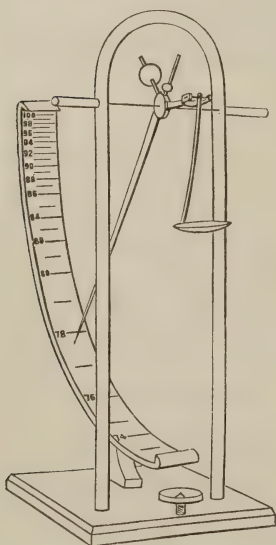


FIG. 4

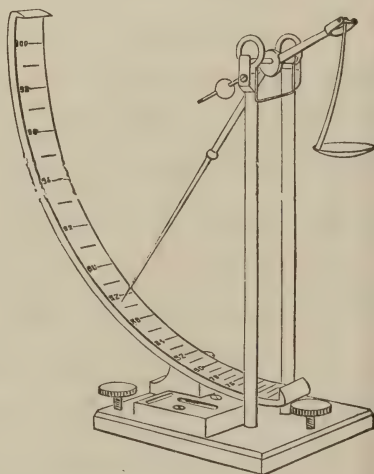


FIG. 5.

also eventually a molecular change takes place in the spring itself, for after a time the balance becomes erratic and untrustworthy. Fig. 4 will give the reader an idea of the arrangement.

The defects of this modification made me try the knife edge again, for before this torsion balance was used one fitted with a knife edge had been tried, but, owing to defective design, it was not quite satisfactory, and had drawbacks which the one with the spring had not, and the latter was therefore adopted for the time being in preference to the knife edge.

A further trial with a knife edge succeeded beyond my expectation; the defects of the former attempt were remedied, and now the form is as given in Fig. 5.

To get a sweep of 90° , it was found necessary to use a very acute angled knife, which had to be placed at an angle to the planes, the edge of which knife, however, was kept concentric with the centre of the disc D, as shown in the sketch, Fig. 7 (p. 527). These planes are not planes, but segments of a circle, the same as used in Cotton's automaton balance; this causes the balance to start from the same place each time, no matter how it is knocked about. Further, the knife is kept in position by two steel plates, SP (Fig. 6), set as close to the ends of the knife as possible without touching. The steel parts of these balances are so highly burnished as to appear like mirrors. The scale is made of brass, into which is slipped a strip of diaphanous ivory or hard paper, or, if preferred, the metal may be marked and engraved, in which case a silver scale would give the markings greater contrast. The paper scale, however, has been found to answer admirably. The balance can be adjusted so that zero equals anything from 0 to 10. Seldom do we get gold under 7000 fine, so 0 is made equal to 7000 with us; 60, 50, or any other convenient minimum, depending on the average fineness of the gold under assay, can be selected for zero. The intermediate weights up to fine can be then indicated by placing the ordinary weights in the pan, and making marks on the scale. When once this is done, the arrangement is complete, and no further use of weights with this balance is necessary.

When this apparatus was designed, a pointer 9 inches long was used, with the hope of being able to read to 0.01 grain. This, so far, has not been accomplished. The balance comes to rest in 15 seconds, and can be read in 10 seconds. This is quite fast enough, but it can be made to come to rest more quickly by attaching a flat plate to the pointer.

When, say, No. 1 cornet is being weighed on the ordinary assay balance, No. 2 will be on the auxiliary one, and when No. 2 is removed to the ordinary balance, No. 3 will be indicating its weight, and so on; no time, therefore, is lost, except in the extra handling, which,

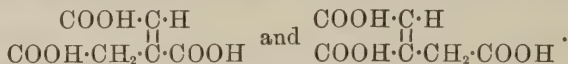
as already pointed out, becomes so mechanical that really the time saved far more than compensates for this extra shifting, the result being greater speed with less concentrated attention.

*Royal Mint,
Melbourne.*

XXXVIII.—Contributions to the Knowledge of Ethylic Acetoacetate. Part I. Acetonylmalic acid.

By SIEGFRIED RUHEMANN, Ph.D., M.A., and E. A. TYLER, Scholar of St. John's College, Cambridge.

CORRESPONDING with the formula for aconitic acid, there are two configurations which may be represented by the following symbols.

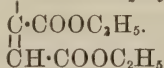


The study of citrazinamide, the product of the interaction of ethylic aconitate* with ammonia, led to the conclusion that the known aconitic acid is to be represented by the first expression (Ruhemann and Orton, *Ber.*, 1894, **27**, 3449). The experiments described in this paper were undertaken with a view of preparing this acid and its stereoisomeride, from fumaric and maleïc acids.

With this object, we studied the action of the ethereal salts of their chlorinated derivatives on the sodium derivative of ethylic acetoacetate, in the hope of arriving at the stereoisomeric ethylic



acetylaconitates,



In both cases, however, we

* In preparing citrazinamide by the action of ammonia on ethylic aconitate, I always found that in using the ethereal salt obtained by Hentschel's method (*J. pr. Chem.*, 1887, **35**, 205), a small quantity of a substance was formed which does not dissolve in ammonia, and which can, therefore, be easily separated from the pyridine derivative. The product readily dissolves in boiling alcohol, and crystallises from the solution in colourless needles, melting at 136°; it does not contain nitrogen, and on analysis gave numbers, which agree with the formula, $\text{C}_{19}\text{H}_{28}\text{O}_{20}$.

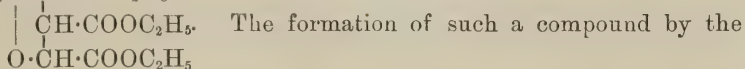
0·1982 gave 0·3996 CO_2 and 0·1206 H_2O . C = 54·98; H = 6·76.

0·1720 „ 0·3450 CO_2 „ 0·1050 H_2O . C = 54·70; H = 6·78.

$\text{C}_{19}\text{H}_{28}\text{O}_{20}$ requires C = 54·80; H = 6·73 per cent.

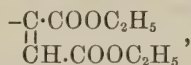
This substance is undoubtedly the ethereal salt of an acid, formed along with aconitic acid by the action of sulphuric acid on citric acid, but the amount at my disposal did not enable me to further investigate it. I intend, however, at some future date, to study the conditions under which this acid may be obtained in larger quantity.—S. R.

found that one and the same compound was formed having the formula $C_{14}H_{20}O_7$; this result indicates that a different constitutional formula must be assigned to it, and its chemical behaviour points to the same conclusion. The ethereal salt is insoluble in potash, it does not yield a hydrazone on treatment with phenylhydrazine, nor is it decomposed with formation of aconitic acid on boiling with either an aqueous or an alcoholic solution of potash. The properties of the substance indicate a compound of the formula

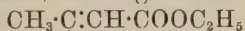


action of the ethereal salts of chlorofumaric and chloromaleïc acids on the sodium derivative of ethylic acetoacetate is easily interpreted on the basis of the knowledge of the chemical behaviour of ethylic acetoacetate, which we owe to the researches of Michael and of Claisen. These researches led to the conclusion that, under certain influences, the ketone-group, $-\text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$, suffers a transformation into the ethenol-group, $-\text{C}(\text{OH}) : \text{CH} \cdot \text{COO}_2\text{H}_5$, and this change takes place readily if negative groups are substituted in the molecule of the ethereal salt, thus leading to compounds of the formula $-\text{C}(\text{OR}) : \text{CH} \cdot \text{COOC}_2\text{H}_5$. The conclusions which follow from the chemical behaviour of ethylic acetoacetate and its derivatives have found a welcome confirmation in W. H. Perkin's interesting work on the magnetic rotation (*Trans.*, 1892, **61**, 1800), and in that of Brühl on the refractometric behaviour of those compounds (*Ber.*, 1892, **25**, 366, and *J. pr. Chem.*, 1894, **50**, 119).

The above researches enable us to give the following interpretation of the action of the ethereal salt of chlorofumaric acid on the sodium derivative of ethylic acetoacetate. The negative group,

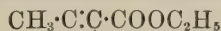


contained in the former salt, entering into the molecule of ethylic acetoacetate, would give rise to the formation of a compound of the



formula $\begin{array}{c} \text{O} \cdot \text{C} \cdot \text{COOC}_2\text{H}_5 \\ || \\ \text{CH} \cdot \text{COOC}_2\text{H}_5 \end{array}$. The fact that the same substance is

produced on using ethylic chloromaleate leads to the conclusion that at the same time a molecular transformation takes place with the



formation of the ring compound, $\begin{array}{c} | \\ \text{CH} \cdot \text{COOC}_2\text{H}_5 \\ | \\ \text{O} \cdot \text{CH} \cdot \text{COOC}_2\text{H}_5 \end{array}$. The product

appears, thus, as a derivative of furfuran, and it may be regarded as ethylic methyldihydrofurfurantricarboxylate. This view of the

constitution of the compound, is supported by its chemical properties, agrees with its spectrometric behaviour, and furnishes a ready explanation of the transformation which the ethereal salt suffers under the influence of alcoholic potash. The hydrolysis of this salt is accompanied by a change which results in the formation

of acetonylmalic acid, $\text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\underset{\text{CH}(\text{OH})\cdot\text{COOH}}{\text{CH}}\cdot\text{COOH}$. The acid

would appear as a compound containing the ethenol-grouping; this view is supported by the above-mentioned researches on the behaviour of ketone compounds (compare Claisen, *Ber.*, 1892, 25, 1760, 1776).

EXPERIMENTAL.

Action of Ethylic Chlorofumarate on Ethylic Acetoacetate.

Ethyl chlorofumarate was prepared according to Perkin's direction, namely, adding alcohol to the product of the action of phosphorus pentachloride on tartaric acid; it distils at 127° under a pressure of 10 mm. 47.6 grams of this ethereal salt are gradually added to a solution of the sodium derivative of ethylic acetoacetate, obtained by mixing 30 grams of the ethereal salt with a solution of 5.4 grams of sodium in 150 grams of absolute alcohol. The action is completed after half an hour's heating on the water bath in a flask fitted with a reflux condenser. On removing the alcohol by distillation and adding water to the residue, an oil is thrown down, which, when washed with water and dried over calcium chloride, boils at $188-189^\circ$ under a pressure of 15 mm. The yield amounted to 50 grams.

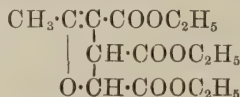
On analysis, it gave numbers corresponding with the formula $\text{C}_{14}\text{H}_{20}\text{O}_7$.

0.2154 gave 0.4380 CO_2 and 0.1298 H_2O . C = 55.45; H = 6.64.

0.1897 „ 0.3884 „ 0.1154 „ C = 55.84; H = 6.75.

$\text{C}_{14}\text{H}_{20}\text{O}_7$ requires C = 56.0; H = 6.67 per cent.

The density determination of the ethereal salt gave $d_{16^\circ/16^\circ} = 1.1580$. This compound, as pointed out before, is to be regarded as ethylic methyldihydrofurfurantricarboxylate. The formula



is supported by the spectrometric behaviour of the substance. Mr. L. R. Wilberforce, demonstrator at the Cavendish Laboratory, had the kindness to determine the refractive index of the compound, which he found to be $n_{\text{Na}} = 1.470$. The molecular refraction, $M \frac{n^2 - 1}{(n^2 + 2)d}$,

amounts, therefore, to 72.30, whilst (using Conrady's numbers) the formula $C_{14}H_{20}O_4 < O''_3$ requires 71.94.

The ethereal salt is insoluble in potash, and, as mentioned before, does not yield a hydrazone on treatment with phenylhydrazine. The constitution of the product formed by the interaction of ethylic chlorofumarate and the sodium derivative of ethylic acetoacetate is also in agreement with the behaviour of the compound towards ammonia and alcoholic potash.

Action of Ammonia.—On allowing the ethereal salt to remain in contact with strong aqueous ammonia, the oil entirely disappears after a few hours, and the solution darkens and deposits long needles, which gradually increase in quantity, transforming the contents of the vessel into a semi-solid mass. The crystals are collected, and the adhering dark coloured mother liquor removed by washing with a little water. The substance readily dissolves in boiling water, and crystallises from the solution in long, colourless needles, which melt at 195° .

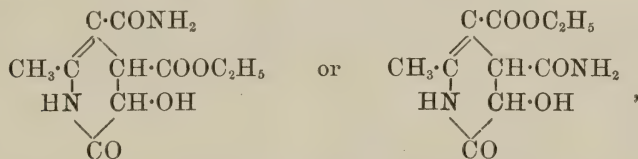
On analysis the following numbers were obtained, which correspond with the formula $C_{10}H_{14}N_2O_5$.

0.2096 gave 0.3832 CO_2 and 0.1094 H_2O . C = 49.86; H = 5.80.

0.1938 „ 18.8 c.c. moist nitrogen at 12° and 770 mm. N = 11.66.

$C_{10}H_{14}N_2O_5$ requires C = 49.586; H = 5.785; N = 11.56 per cent.

The constitution of the compound $C_{10}H_{14}N_2O_5$ is most probably represented by the symbol



and the substance is to be regarded as the monamide of ethylic methylhydroxydihydropyridonedicarboxylate. Its formation from the furfuran derivative by the action of ammonia may be explained by assuming that first an addition of water with accompanied destruction of the furfuran-ring takes place, analogous to the decomposition which is brought about by potash, and that then ammonia causes a condensation to the pyridine compound.

Action of Potash.—The ethereal salt is readily decomposed by boiling it with an alcoholic solution of potash; after about two hours' heating, the alcohol is distilled off, the residue dissolved in water, and the solution after adding excess of hydrochloric acid, is repeatedly extracted with ether. On evaporating the ether, an oil is left, which, after standing for a day, solidifies to a mass of colourless, transparent

rhombohedra; these are exceedingly soluble in water, and, after recrystallisation from it, melt at 145—146°.

Analysis of the acid, dried in a vacuum over sulphuric acid, leads to the formula

$$\begin{array}{c} \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH} \\ | \\ \text{CH}(\text{OH})\cdot\text{COOH} \end{array}$$

0.2108 gave 0.3400 CO₂ and 0.0997 H₂O. C = 43.98; H = 5.25.

C₇H₁₀O₆ requires C = 44.21; H = 5.26 per cent.

On titration of the acid, it was found that a solution of 0.1901 gram was neutralised by 19.6 c.c. of a normal soda solution, instead of 20 c.c. as required for a dibasic acid of the formula C₇H₁₀O₆.

A warm aqueous solution of the acid is coloured red by ferric chloride. The salts which acetonylmalic acid forms with the alkalis and alkaline earths are very soluble in water.

The *barium salt*, prepared by boiling the aqueous solution of the acid with barium carbonate and adding alcohol to the concentrated filtrate, is a white, hygroscopic powder, which is exceedingly soluble in water. The salt, when dried at 110°, seems to have the composition C₇H₈BaO₆H₂O, as indicated by the following determination.

0.2554 gave 0.1744 BaSO₄. Ba = 40.15.

C₇H₈BaO₆ + H₂O requires Ba = 39.94 per cent.

The *silver salt* gradually separates as a white, crystalline powder on adding silver nitrate to a solution of the acid neutralised by ammonia. It is readily soluble in boiling water, and is not acted on by light, neither is it altered on drying at 100°.

On analysis, it gave numbers corresponding to the formula C₇H₈Ag₂O₆.

0.2200 gave 0.1176 Ag = 53.45.

0.2136 „ 0.1140 „ = 53.55.

C₇H₈Ag₂O₆ requires Ag = 53.46 per cent.

Phenylhydrazine Salt.—Phenylhydrazine acts on the acid with the formation not of a hydrazone but of a salt. This gradually separates from the alcoholic solution of the acid, on adding hydrazine to it, in clusters of colourless needles, which are sparingly soluble in cold alcohol, but readily on boiling. The compound is characterised as a salt of phenylhydrazine by the results of the analysis, and by the fact that it readily reduces Fehling's solution, and is decomposed by dilute potash.

A nitrogen determination gave the following number, which agrees with that required by the formula C₇H₁₀O₆.2NH₂.NH.C₆H₅.

0.2028 gave 25 c.c. moist nitrogen at 19° and 750 mm. N = 13.97.

C₁₉H₂₆N₄O₆ requires N = 13.79 per cent.

Action of Ethylic Chloromaleate on Ethylic Acetoacetate.

The chloromaleic acid was prepared by distilling chlorofumaric acid, and by dissolving the resulting anhydride in water (Perkin, *Trans.*, 1888, **53**, 695). In the distillation, part of the chlorofumaric acid passes over unchanged, together with chloromaleic anhydride, as already observed by Kauder (*J. pr. Chem.*, 1885, **31**, 1); the purification is brought about by distillation under diminished pressure, when the chlorofumaric acid remains behind (Zincke, *Ber.*, 1893, **26**, 508). The ethereal salt of chloromaleic acid, obtained, according to Perkin's direction, by the action of ethylic iodide on the dry silver salt, boils at 122° under a pressure of 15 mm.

Ethylic chloromaleate acts on the sodium derivative of ethylic acetoacetate as readily as the derivative of fumaric acid does, giving rise to the formation of the same compound as that obtained from chlorofumaric acid. It boiled at 187 — 188° under a pressure of about 15 mm., and gave on analysis the following numbers.

0.2196 gave 0.4507 CO_2 and 0.1306 H_2O . C = 55.97; H = 6.60

$\text{C}_{14}\text{H}_{20}\text{O}_7$ requires C = 56.0; H = 6.67 per cent.

The determination of the density of the ethereal salt gave the following result. $d_{12^{\circ}/12^{\circ}} = 1.1588$; the refractive index was found by Mr. Wilberforce to be $n_{\text{Na}} = 1.470$.

The identity of the product formed from ethylic chloromaleate with that from the corresponding derivative of fumaric acid, which is proved by its physical properties, follows also from the chemical behaviour. Ammonia acts on the substance obtained from the ethereal salt of chloromaleic acid with formation of a compound of the formula $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_5$, the identity of which, with the product resulting from ethylic chlorofumarate, is proved by the melting point (195°) and by a nitrogen determination.

0.200 gave 21 c.c. moist nitrogen at 18° and 732 mm. N = 11.66.

$\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_5$ requires N = 11.56 per cent.

We are at present engaged in the further study of the compounds described in this paper, and hope shortly to communicate the result to the Society.

*Gonville and Caius College
Cambridge.*

XXXIX.—*Analysis of the Water from the Dropping Well at Knaresborough, in Yorkshire.*

By BENJAMIN ARTHUR BURRELL.

THE history of Knaresborough dates from before the Norman Conquest, and the remarkable petrifying qualities of this spring must have attracted attention at a very early period. Its character was well known in 1534, for Leland thus describes it (*Leland's Itinerary*):—

“A little above March Bridge, but on the farther ripe of Nidde as I cam, is a Welle of a wonderful nature, caullid Dropping Welle, for out of the great Rokkes by it, distilleth water continually ynto it. This water is so could, and of such a nature, that what thing soever faullith oute of the Rokkes ynto this pitte, or ys caste in or growith about the Rokke and is touched of this water, growith ynto stone; or else some sand, or other fine ground that is about the Rokkes, cummith doune with the continuall dropping of the Springs in the Rokkes, and cleavith on such things as it taketh, and so cleavith aboute it and giveth it by continuance the shape of a stone. There was ons, as I hard say, a conduct of stone made to convey water from this welle over Nidde to the priory of Knaresborough; but this was decayed afore the dissolution of the house.”

It would, therefore, appear that some time prior to 1534, the water was used for drinking purposes.

From 1626 up to as late as 1838, it had a considerable reputation as a spa water, and numerous references as to its medicinal qualities are to be found in the works of Short, Elliott, Walker, and Hunter.

Dr. Short, in 1734, found it “to be twenty-four grains in a pint heavier than common water, on exhaling eighteen pints it left seventeen scruples of sediment.”*

In 1783, Dr. Walker states, “the petrefying spring at Knaresborough contains a considerable quantity of *selenitical*, and a smaller quantity of *calcareous earth*.”†

This water was analysed in 1830, by Mr. W. West, of Leeds. His numbers were‡

* *The Natural, Experimental, and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire, and Yorkshire.* By Thomas Short, M.D., of Sheffield. London, 1734.

§† *An Essay on the Waters of Harrogate and Thorp Arch in Yorkshire.* By Joshua Walker, M.D. London, 1784.

‡ *The Waters of Harrogate and its Vicinity.* By Adam Hunter, M.D. London, 1830; also, *On Mineral Springs and other Waters of Yorkshire.* By W. West. *British Association Report*, 1844.

<i>Saline Contents in grains per Imperial Gallon:—</i>		<i>Gases yielded by the Water in Cubic Inches per Imperial Gal- lon:—</i>	
Carbonate of lime	23	Carbonic acid	7
Sulphate of lime	132	Azote	8
Sulphate of magnesia	11	Oxygen	1
Carbonate of soda	6		—
Iron	trace	Total	16
Solid contents on evapora- tion	} 172	Sp. gr. of water = 1.0032.	—

So far as I am aware, no analysis has been made since 1830, and it seemed very desirable that a more complete examination should be made of this curious water. The investigation was commenced in 1894, and extended over the following year, various samples of the water having been taken from time to time.

The strata on which Knaresborough is built is mostly magnesium limestone. The Dropping Well is situated in the Long Walk, on the south-west bank of the river Nidd, where the water rises in the steep declivity of a hill, at the foot of a limestone rock, and flows in a small stream for about 24 yds. It is then caused to spread over the surface of a large rock, some 30 ft. high and 32 ft. long, over which it trickles. The upper part of this rock projects considerably over the base, and it is to this projection that the articles to be petrified are hung.

The water for analysis was collected immediately as it issues from the ground; at this point it is very clear and free from suspended particles. The flow is about 20 gallons a minute, and the temperature very constant, two readings giving

August Temp. of air, 15.5° C.; temp. of water, 9.7° C.
December „ 2.0° C.; „ 9.0° C.

The specific gravity = 1.0024 at 15.5°; it was taken by means of a Sprengel tube, the capacity of which had been very carefully determined. In each case the determination was made the same day as that on which the water was collected.

Analysis.—The general course adopted was that recommended by Fresenius; the numbers given are the means of at least two, and in some cases three or more concordant results. For the estimation of substances present in minute quantity, 25 litres were evaporated, but no traces of bromine, iodine, fluorine, or lithium could be detected.

Strontium was separated by the Rose-Stromeyer process, which has been carefully examined by Fresenius (Abstracts, 1893, ii, 301), who finds it to give very perfect results. The method was checked by making up mixtures of calcium and strontium sulphates in proportions similar to those found in the well water, the results

obtained show that the process is trustworthy. In each estimation, the separated strontium sulphate was subjected to spectroscopic examination, but contained only the merest trace of admixed calcium sulphate.*

In estimating the gases dissolved in the water, the apparatus devised by Sidney Harvey was employed (*Analyst*, 1894, **19**, pp. 121, 122, 123); by means of this apparatus, the water may be collected at the source in the bulb in which it is afterwards boiled, thus reducing contact with the atmosphere to a minimum.

The atomic weights used are those given in Clowes and Coleman's *Quantitative Analysis*, 1894.

In the first table, the quantities of the different constituents are given in grams per litre under I, and in grains per gallon under II. In III the acids and bases are combined together, and the results stated in grains per gallon; and Table IV gives the gases dissolved in the water.

Constituents per Litre and per Gallon.

	I. In grams per litre.	II. In grains per gallon.
CO ₂	0.1614	11.298
SiO ₂	0.0107	0.749
SO ₄	1.3524	94.668
Cl	0.0270	1.890
Fe.....	0.0011	0.077
Mn.....	0.0006	0.042
Ca	0.6330	44.310
Sr	0.0046	0.322
Mg	0.0491	3.437
Na	0.0156	1.092
K	0.0035	0.245
NH ₃	0.00002	0.0014
Al.....	trace	trace
P ₂ O ₅	trace	trace
HNO ₂	none	none
HNO ₃	none	none

In combining the various acids and bases, a deviation from the usual course has been adopted, the sulphuric acid being first combined with the magnesium in preference to the calcium, as practically the whole of the magnesium was found in the boiled water, and none in the sediment thrown down on boiling.

* For the occurrence of strontium sulphate at Knaresborough the following may be consulted: *Trans. Geological Society*, 1817, **4**, 445; *Edinburgh Phil. Journal* Jan. 1825, **12**, 178, 179.

III. *Dissolved Saline Constituents in grains per gallon:—*

Calcium sulphate....	114.373
Calcium carbonate...	25.480
Calcium silicate	1.442
Strontium sulphate ..	0.672
Magnesium sulphate .	17.003
Ferrous carbonate ...	0.154
Manganous carbonate	0.084
Sodium chloride	2.765
Potassium chloride...	0.462
Alumina	trace
Phosphoric acid.	„

162.435

Fixed residue by evaporation dried at } 162.324
170—180°

Sp. gr. at 15.5°..... 1.0024

IV. *Gases dissolved by the Water in cubic inches per gallon, and measured at 15.5° and 760 mm.*

Carbon dioxide.....	4.74
Oxygen	1.29
Nitrogen*	5.02
Total	11.05

* Not examined for argon.

It should be stated that all the reagents used in the analysis were not only of the highest degree of purity obtainable, but were carefully tested, the impurities estimated, and (as measured quantities were used throughout) allowed for in the final results.

It is intended to make the analysis of the deposit or sinter the subject of a future paper.

XL.—*Charas. The Resin of Indian Hemp.*

By T. BARLOW WOOD, M.A., W. T. NEWTON SPIVEY, M.A., and THOMAS HILL EASTERFIELD, M.A., Ph.D.

SEVERAL preparations of *Cannabis indica* (syn. *sativa*), differing in physiological activity and in the manner of application to the human subject, are familiar to the Eastern nations. Of these, “charas” is an Indian drug, and is regarded by the natives as the most potent substance obtainable from the plant. It is chiefly used in the Punjab, and consists essentially of the resinous exudation from the stems, leaves, and flower heads of the unfertilised female plant. By the kindness of Mr. Charles A. Silberrad, B.A., I.C.S., at present resident at Etawah, N.W.P., the authors have been provided with several pounds of the resin, the examination of which has furnished the materials for the present communication.

Cannabis indica has been employed medicinally, both in this country

and on the Continent, but the uncertain action of the drug has prevented its use from becoming general, different preparations having apparently very different effects on the organism. It was with the object of isolating the physiologically active constituent of the hemp plant that the present research was undertaken, the importance of cannabis in veterinary medicine having been pointed out to the authors by Professor F. R. Hobday, of the Royal Veterinary College, and Mr. W. A. Wood, M.R.C.V.S.

Charas was examined rather than any other preparation because the active principle appeared to be most highly concentrated in this natural exudation, and also because it contains no chlorophyll, a substance which causes much inconvenience in the examination of extracts made from the plant itself.

Now that the characteristic compound has been isolated by the authors and placed in the hands of experienced pharmacologists, the difficulties which have hitherto attended the pharmaceutical use of Indian hemp will probably disappear.

More than 40 original papers referring to *Cannabis indica* have been published; abstracts of these are to be found in a dissertation by Leib Lapin (*Zur Kenntniss der Cannabis indica*, Jurjew, 1894), and in the *Journal of the Imperial Institute*, vol. ii, No. 15, 105 (March, 1896).

The physiological action was ascribed by T. and H. Smith (*Pharm. Jour.*, 1847, **6**, 675) to a resin which they obtained by alcoholic extraction of the dry plant, previously treated with acid and alkali, evaporation with lime to destroy chlorophyll, and subsequent extraction of the mass with alcohol. No definite composition was assigned to the resin; it could evidently have contained no alkaloids.

Personne (*J. Pharm.*, 1857, **31**, 47) attributed the physiological effect to a volatile oil, whilst various observers have stated, and others have denied, that an alkaloid is present in the plant. The authors would state that their results do not agree with those obtained by any one investigator. Personne's volatile oil has been shown by Valenta (*Gazzetta*, 1889, **10**, 540), and more recently by Vignolo (*Gazzetta*, 1895, **25**, i, 110), to be an impure sesquiterpene. This substance is also present in "charas," but is comparatively inert. Smith's resin contains the active substance in large quantity, but is not a pure chemical compound. The authors have separated from charas and from Smith's resin an oil, resinous at ordinary temperatures, and having the formula $C_{18}H_{24}O_2$. This substance is present in charas to the extent of 33 per cent., and in Smith's preparation to nearly 80 per cent., and the authors have been able to isolate the same compound, not only from the ethereal and alcoholic extracts of the dry plant, but also from two commercial preparations by Merck,

of Darmstadt, known as "cannabinon" and "cannabis resin" respectively. Charas has yielded no alkaloïd, but the balance of evidence is in favour of some relatively inert alkaloïdal substance being present in small quantity in Indian hemp.

Since the compound $C_{18}H_{24}O_2$ gives rise to all the symptoms of cannabis poisoning, such as is produced amongst the "haschish" smokers, the authors are of opinion that the main effects produced by the drug are due to the action of this substance, but that the presence of the terpenes and other constituents probably causes secondary effects, which to a certain extent interfere with the highly characteristic physiological action for which Indian hemp is so noted.

The ethereal extract from charas has yielded four distinct chemical compounds.

1. A terpene, boiling at $160-180^\circ$. Yield 1.5 per cent.
2. A sesquiterpene, boiling at $258-259^\circ$. Yield 2 per cent.
3. A paraffin ($C_{29}H_{60}$), m. p. $63-64^\circ$. Yield 0.15 per cent.
4. A toxic red oil, $C_{18}H_{24}O_2$, boiling at 265° under a pressure of 20 mm. Yield 33 per cent. of the charas taken.

EXPERIMENTAL.

Two kilos. of charas were extracted completely with ether, the ethereal extract concentrated to a syrup, and the product distilled until the thermometer rose to 300° ; the residue was then distilled under a pressure of 15—60 mm., when the whole, with the exception of a pitchy residue, came over between 270° to 290° .

The charas was thus separated into four crude products.

- A. The portion insoluble in ether, 755 grams, that is, 38 per cent.

This was a grey powder containing much ash, and about 3 per cent. of nitrogen. On destructive distillation, it yielded ammonia, pyrroline (pine-shaving reaction), and organic bases. No alkaloïd was obtainable by the usual methods of extraction, and it has not been further examined. Under the microscope it was seen to be largely composed of plant hairs.

- B. The oily distillate from the ether extract, boiling below 300° .
Weight, 200 grams = 10 per cent.

- C. The red resinous portion boiling at $270-290^\circ$, under a pressure of 15—60 mm. Weight, 650 grams = 33 per cent.

- D. The pitchy residue. Weight, 160 grams = 8 per cent.; this was not further examined.

Examination of Fraction B.

1. *Terpene of Low Boiling Point.*—The oil was distilled until the temperature rose to 200° ; the distillate was shaken with water, dried

with calcium chloride, and then repeatedly fractionated over sodium, and finally over phosphoric anhydride. 30 grams of an oil boiling between 160° and 180° , and mostly coming over between 165° and 175° , was thus obtained. The portion distilling between 170 and 175° was analysed.

Calculated for $C_{10}H_{16}$, $C = 88.2$; $H = 11.8$.

Found, $C = 87.8$; $H = 12.0$.

The vapour density by Victor Meyer's air displacement method was found to be 65. Calculated for $C_{10}H_{16} = 68$.

The sp. gr. of the oil at $17^{\circ}/4^{\circ}$ was found to be 0.819, which is considerably less than that of the ordinary terpenes. It is slightly lævorotatory, but in consideration of the very doubtful purity of the substance no importance could be attached to a determination of the specific rotation. The oil has a very pleasant terebinthous odour, and resinifies with remarkable rapidity on exposure to the air. It combines with hydrogen chloride to form an oily monohydrochloride (found, 22 per cent. Cl.; calculated, 20.6), the first few bubbles of gas giving rise to a brilliant violet coloration.

The same compound, boiling at 160 — 180° , has been found by the authors in an ethereal extract of the plant supplied to them by Merck. It was isolated by steam distillation, &c.

Monoterpenes have not been previously reported amongst the products obtained from the hemp plant.

Terpene of High Boiling Point (Sesquiterpene).—That portion of fraction B which boiled above 200° was distilled with steam; a grass-green oil passed over, leaving a less volatile residue (see C below). The green oil was separated from the water by means of ether, dried with calcium chloride, and fractionated. After repeated distillation over sodium, about 35 grams of a colourless oil boiling at 258 — 259° was obtained. The substance is a sesquiterpene.

Calculated for		Found.		
$(C_{10}H_{16})_x$.		I.	II.	III.
C	88.2	87.94	87.60	87.86
H	11.8	11.60	11.73	—

Two vapour density determinations by Hofmann's method at the temperature of boiling nitrotoluene (223°) gave 99.8 and 101.8. Calculated for $C_{15}H_{24}$, vapour density = 102.

The sp. gr. of the freshly distilled oil was 0.898 at 18° , the specific rotation -8.6 at the same temperature. This oil is evidently identical with that isolated by Valenta (*Gazzetta*, 1880, **10**, 540), and more recently by Vignolo (*Gazzetta*, 1895, **25**, i, 110), as a constituent of "cannabene," the oil which Personne obtained by distil-

ling the hemp plant with water. Valenta gives the boiling point as 256—258°, sp. gr. at 0° = 0.9289, and sp. rotation in chloroform solution = -10.81.

The sesquiterpene absorbs hydrogen chloride with production of a violet colour and separation of a brown, tarry mass. Bromine added to a chloroform solution of the compound gives rise to a violet colour, changing to red on adding more of the reagent. Sulphuric acid added to the acetic acid solution at once gives a deep red coloration. The sesquiterpene obtained by Wallach (*Annalen*, 1887, **238**, 81) from oil of cubebs gives a somewhat similar reaction.

Examination of Fraction C.—(1) *Paraffin*, $C_{29}H_{60}$?—The resinous oil which remained when fraction B was steam distilled was added to C, and the mass on standing became filled with white crystalline scales; the whole was then dissolved in boiling alcohol and allowed to cool, when the crystals again separated and were collected. After several recrystallisations from much boiling alcohol, they melted at 63.5—64°, and the melting point was not changed by further recrystallisation. The boiling point was 285—290° under a pressure of 15 mm. Analysis indicated that the substance was a higher paraffin.

	Calculated for $C_{29}H_{60}$	Found.		
		I.	II.	III.
C	85.3	85.15	84.9	84.7
H	14.7	14.54	14.7	15.0

The numbers would agree equally well for any of the higher paraffins. Since, however, the melting and boiling points coincide with those which can with a high degree of certainty be predicted by interpolation for normal nonacosane, $C_{29}H_{60}$ (Krafft, *Ber.*, 1882, **15**, 1702, *et seq.*), there is greater probability that it is this hydrocarbon than that it is any other.

By constructing a curve from the melting and boiling points given by Krafft and interpolating for the unknown members of the paraffin series, the figures obtained are

	Calculated for $C_{29}H_{60}$	Found.
M. p.	63—64	63.5—64
B. p. (15 mm. pressure)	285—286	285—290 (corr.).

The molecular weight by Raoult's freezing point method in naphthalene was found to be 391. Calculated for $C_{29}H_{60}$ = 408.

This hydrocarbon had no action on acid solution of potassium permanganate at 80°, and in chloroform solution it did not absorb bromine from bromine water. Lack of material has prevented a more thorough investigation of the compound.

The authors have isolated the same hydrocarbon from *Resina Cannabis indicæ* as supplied by Merck; from the *Extractum Cannabis indicæ spirit. sicc.* of the German Pharmacopœia; and also from the ethereal and carbon bisulphide extracts prepared from the plant.

A paraffin whose composition and melting point agree with those of the substance under consideration has been found by Zugo (*Gazzetta*, 1889, **19**, 210) in the flowers of *Chrysanthemum cinerariæfolium*, but the authors have had no opportunity of comparing the two substances. An olefine (?) with the same melting point has been found in the flowers of *Anthemis nobilis* (*Naudin Bulletin*, **41**, 484). With the exception of normal heptane, found by Thorpe (*Annalen*, 1879, **198**, 364) in the turpentine of *Pinus sabiniana*, these appear to be the only recorded instances of the occurrence of paraffinoid hydrocarbons in the vegetable kingdom.

Persoune appears to have first noticed the occurrence of a solid hydrocarbon in the hemp plant. He named it hydride of cannabene, and assigned to it the formula $C_{12}H_{14}$ (old notation). No analysis is given in the paper. The same hydrocarbon has been examined by Arutinianz, who describes it as a white substance melting at 60° . His analysis gave $C = 83.81$, $H = 14.58$, only adding up to 98.39. The authors would mention that, unless burnt with extreme care, the substance invariably gives very low results when analysed.

(2.) *Toxic Red Oil*, $C_{18}H_{24}O_2$, *Cannabinol*.—The alcoholic filtrate from the paraffin just described was concentrated, and the syrup distilled under diminished pressure; an oil, amber coloured when seen in thin layers, but ruby red when seen in mass, distilled between 270° and 290° , under a pressure of 15–35 mm. There was practically no residue. Two kilos. of charas yielded upwards of 600 grams of this oil. On redistillation, the compound was found to boil constantly at 265° (20 mm. pressure), 300° (46 mm.), and 315° (1.0 mm.).

When the oil was cooled below 60° , it set to a sticky, semi-solid, odourless mass, insoluble in water, but dissolving easily in alcohol, ether, benzene, glacial acetic acid, and organic solvents generally. Its solution in cold concentrated sulphuric acid is cherry red. Four different preparations were analysed.

		Found.			
		I.	II.	III.	IV.
Calculated for					
$C_{18}H_{24}O_2$.					
C.....	79.4	78.9	79.0	79.3	79.4
H.....	8.8	9.0	9.05	8.9	9.29

Preparation I had been obtained by the use of "petroleum ether," II and III, by ether as described above. IV had been worked up from residues, and had been exposed to the air for some weeks before being analysed. The molecular weight of the oil in acetic acid

solution was found by Raoult's freezing-point method to be 273 and 278. The formula, $C_{18}H_{24}O_2 = 272$. The sp. gr. was found to be 0.9892 at 100°; 1.00925 at 65° and 1.0424 at 18°.

The substance is extremely stable, but it reacts with bromine and with phosphorus pentachloride at the ordinary temperature. Fuming hydriodic acid, with phosphorus, is apparently without action on it below 150°, whilst above this temperature, a mixture of hydrocarbons is formed. Boiling alcoholic potash does not act on the substance and no oxime or phenylhydrazine derivative has been obtained; a monacetyl and a monobenzoyl derivative, however, have been prepared. Experiments on the constitution of the compound are in progress.

The physiological effects of the substances isolated from charas, have been investigated by Dr. C. R. Marshall, assistant to the Downing Professor of Medicine. A full account of the experiments will be published elsewhere, but the following report has been kindly supplied for insertion in the present paper.

"The physiological action of the terpenes closely resembles that of the other members of this class, of which ordinary turpentine may be taken as the type. In doses of 0.5 gram they have very little effect and produce none of the characteristic symptoms of cannabis action. The red oil, on the contrary, is extremely active, and taken in doses of 0.05 gram induces decided intoxication followed by sleep. The symptoms produced by it are peculiar to *Cannabis indica*, and as none of the other products appear to possess this action, this substance must be regarded as the active constituent of the plant."

If the physiological action of hemp is really due to the red oil, it is evident that the oil must exist to a greater or less extent in all the pharmaceutical preparations which are known to exert the characteristic effects. The authors have, therefore, examined a number of such preparations and have in every case succeeded in isolating the compound in question. The approximate yields obtained together with the analytical numbers are recorded in the following table.

Source.	Charas.	Cannabin (Smith's resin).	Cannabinon (Merck).	Ethereal extract (Merck).	Cannabis resin (Merck).
Yield of red oil per cent.	33	80	50	26	20
Calculated for $C_{18}H_{24}O_2$					
C..... 79.4	79.15	79.3	79.4	79.9	77.7
H..... 8.8	9.06	9.6	9.6	9.6	9.3

The oil was also obtained in small quantity from the alcoholic extract (*Extractum Sicc. Pharm. Germanica*) supplied by Merck.

The following notes on the method of treatment pursued in each case may be of use to subsequent workers.

Cannabin (*Smith's Resin*).—The substance was merely distilled under diminished pressure and the distillate once redistilled.

Cannabinon (*Merck*).—The crude material was dissolved in ether, washed with 10 per cent. sodium carbonate solution which removed a small quantity of a non-crystalline acid, then with dilute sulphuric acid, and finally with water. The ethereal solution was concentrated, and distilled under diminished pressure. The distillate had a strong odour of tobacco which was almost entirely removed by steam distillation. The product was finally redistilled. The original cannabinon contained 1.7 per cent. of nitrogen.

Ethereal Extract (*Merck*).—Steam distillation removed the terpenes, the residue was dissolved in alcohol and evaporated with lime, the cake boiled out with spirit, and the solution concentrated and distilled under diminished pressure.

Cannabin Resin (*Merck*).—The dark-green mass was distilled under diminished pressure, and the product repeatedly redistilled. The sample of red oil thus prepared was far from pure as shown by its persistent smell, its fluidity, and the analytical figures.

The red resinous oil has not previously been isolated as a definite chemical compound, although Leib Lapin (*Dissertation Jurgew*, 1894) obtained a substance to which he assigned the formula $C_8H_{12}O$ by a tedious process of fractional precipitation from the ethereal extract of the plant. As far as can be judged from the properties as described by him, his substance may well have been an impure preparation of the red oil. The name, "cannabindon," which Leib Lapin proposes for his substance, from its similarity to "cannabinon," does not recommend itself to the authors who propose the name *cannabinol* as the compound is undoubtedly a hydroxyl derivative.

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XLI.—*The Constitution of a new Dibasic acid, resulting from the Oxidation of Tartaric Acid.*

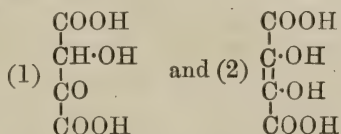
By HENRY J. HORSTMAN FENTON, M.A.

WHEN tartaric acid is oxidised under certain conditions in presence of ferrous iron, a new acid is produced which has powerful reducing properties, and gives beautiful colour reactions with ferric salts. The

conditions of formation, composition, molecular weight, and many transformations and derivatives of this acid have been described in former communications (*Trans.*, 1894, **65**, 899; 1895, **67**, 48 and 774). With regard to the conditions of formation, some experiments have since been made with a view of explaining the fact previously noted, that moist ferrous tartrate when exposed to the air gives rise to a certain quantity of this acid, but that the effect is much more marked if the exposure be made in the open air. This difference is shown to be due to the influence of sunlight, hardly any effect being produced in the dark (*British Assoc. Report*, 1895).

The acid has the formula $C_4H_4O_6, 2H_2O$. It is a beautifully crystalline substance having a pearly lustre, quite permanent in the air at ordinary temperatures, but readily losing its water of crystallisation when heated in an inert atmosphere at a temperature of 60—80°, yielding a white, amorphous powder. It is very sparingly soluble in cold water, but dissolves easily in warm water, and the solution is extremely unstable, splitting up almost quantitatively into glycollic aldehyde and carbon dioxide. Bromine, in presence of water, oxidises it quantitatively to dihydroxytartaric acid, and it is easy in this way to prepare considerable quantities of the latter acid in the free state. Reduction with hydrogen iodide gives, finally, succinic acid, but if the action be limited some form of tartaric acid is produced—probably racemic acid. The action of phenylhydrazine and hydroxylamine on it both give rise to crystalline products. The acid is dibasic, and most of its salts crystallise extremely well.

The object of the present investigation has been to throw light on the constitution of the acid. Having regard to the mode of formation and properties already mentioned, it is evident that only two formulæ are admissible—



The first formula would represent a ketonic acid, having one alcoholic hydroxyl group, resulting from the oxidation of $\text{CH}\cdot\text{OH}$ in tartaric acid to CO . The second indicates an unsaturated acid, containing two alcoholic hydroxyl groups, produced by the abstraction of the two non-hydroxylic hydrogen atoms from tartaric acid. It might assume both of these tautomeric forms, or, if its constitution be represented by the second formula, one would expect two isomeric modifications—the fumaroid and maleinoid.

The readiness with which the acid interacts with phenylhydrazine and with hydroxylamine to produce crystalline compounds appeared

at first sight to indicate the probability of the ketonic formula. These compounds, and the conditions of their productions were, therefore, carefully studied in order to ascertain whether any evidence is afforded of hydrazone or oxime formation.

It was to be expected that the behaviour of acetyl and of benzoyl chloride, and of acetic anhydride, would give important information as to the number of alcoholic hydroxyl groups present. A careful study was, therefore, made of the actions of acetyl chloride on the methylic salt and on the free acid, also of acetic anhydride and of benzoyl chloride on the free acid. Excess of the reagent was employed in all cases, and beautifully crystalline products were obtained, all of which resisted the action of water. As the analytical results obtained in the above experiments left little doubt as to the probability of the second formula rather than the first, the action of aniline was investigated with a view of assigning a fumaric or maleic constitution to the acid; and, finally, the behaviour of hydrogen bromide under various conditions was studied, and most interesting and sometimes unexpected results were obtained.

EXPERIMENTAL.

Action of Phenylhydrazine on the Original Acid.

When excess (3 or more mols.) of phenylhydrazine in either alcoholic or acetic solution is added to a solution of the original acid (1 mol.) in dilute alcohol or acetic acid, in the cold, a beautiful silver-white precipitate appears after a few moments; this consists of flat, oblique plates, and, when collected on a filter, has a most brilliant lustre. It appears to be insoluble, or nearly so, in water, alcohol, ether, or benzene. Dilute sulphuric acid decomposes it, giving back the original acid. Treated with ferric chloride and alkali, it gives no coloration at first, but, on standing for a short time, the characteristic violet colour appears. It turns dark red on heating, and melts at about 140° .

On analysis the air-dried substance gave the following results.

0.2550 gave 0.4928 CO_2 and 0.1226 H_2O . $\text{C} = 52.70$; $\text{H} = 5.34$.

0.1739 „ 23.5 c.c. nitrogen at 17° and 755.3 mm.* $\text{N} = 15.86$.

If the substance is a phenylhydrazine salt, $\text{C}_4\text{H}_4\text{O}_6, 2\text{N}_2\text{H}_3\text{C}_6\text{H}_5$, it would require $\text{C} = 52.74$; $\text{H} = 5.49$; $\text{N} = 15.38$ per cent.

If this substance is kept for a few days, or if it be heated, it turns pale golden-yellow, and eventually becomes dark orange coloured;

* In the nitrogen determinations, throughout this paper, the pressures given are those obtained by subtracting the maximum pressure of the vapour from aqueous potash solution (1 in $2\frac{1}{2}$) from the observed barometric pressure.

yellow and orange products are also obtained when solutions of the acid and phenylhydrazine are heated together for some time. A large number of analyses were made of these yellow and orange products, prepared in different ways, and under various conditions as to temperature, &c. The results were very variable (from $C = 42.49$; $H = 5.26$; $N = 14.83$ to $C = 51.72$; $H = 4.85$; $N = 15.59$), but always lower than those obtained in the analysis of the above salt. These coloured products do not give back the original acid on treatment with sulphuric acid, and they appear to be mixtures of oxidation products or of decomposition products.

Action of Phenylhydrazine on the Methylic and Ethylic Salts.—Neither the methylic nor ethylic salt gives any reaction with phenylhydrazine. Various experiments were made both in alcoholic and acetic solutions, and no apparent change took place in any case, even after prolonged heating.

Action of Hydroxylamine on the Original Acid.

Excess of hydroxylamine hydrochloride in aqueous solution was added to an alcoholic solution of the original acid (in the proportion of about 4 mols. $NH_2 \cdot OH$ to 1 mol. $C_4H_6O_8$). A white, crystalline precipitate began to separate after a minute or two. These crystals have already been described (*loc. cit.*). The crystals were well washed with small quantities of water, and air-dried.

0.2177 gave 0.1830 CO_2 and 0.0929 H_2O . $C = 22.92$; $H = 4.74$.

0.2089 „ 24.1 c.c. nitrogen at 14° and 745 mm. $N = 13.49$.

A normal hydroxylamine salt would require $C = 22.42$; $H = 4.67$;
 $N = 13.08$ per cent.

This salt gives the characteristic violet colour with ferric chloride and alkali. It melts and decomposes almost explosively at $115-117^\circ$, so that much care has to be exercised when analysing it. The crystals soon undergo decomposition, even when kept in a stoppered tube, becoming transformed, after a few weeks, into a black, semi-fluid mass.

No other crystallisable compound could be obtained by using different proportions or by the addition of sodium carbonate or hydroxide, nor could any results be obtained from the *methylic or ethylic salts*, with or without the addition of alkali.

Action of Acetyl Chloride on the Dimethylic Salt.

The recrystallised dimethylic salt was mixed with excess (about 15–20 mols.) of acetyl chloride, and heated on a water bath in a flask connected with a reflux condenser for about 45 minutes; hydrogen chloride was evolved, and a clear liquid was obtained. After

the excess of acetyl chloride had been distilled off, the residue solidified to a crystalline mass on cooling. For purification, two methods were tried: (a) The crystalline residue was kept in a vacuum desiccator for about 20 hours over solid potash and sulphuric acid, and then recrystallised from anhydrous ether; this specimen melted at 93°. (b) The residue was washed with cold water, drained, and recrystallised from boiling water; this specimen melted at 101.5°. From its appearance and melting point, it was evidently purer than the (a) specimen, and was therefore selected for analysis.

1.1561 gave 0.2621 CO₂ and 0.0635 H₂O. C = 45.79; H = 4.51.

0.1344 „ 0.2264 „ 0.0568 „ C = 45.94; H = 4.69.

Theory for a *di*-acetyl derivative, $\begin{array}{c} \text{COOCH}_3 \\ | \\ \text{CO} \cdot \text{COCH}_3 \\ | \\ \text{CO} \cdot \text{COCH}_3 \\ | \\ \text{COOCH}_3 \end{array}$. C = 46.15; H = 4.61

per cent. A *mon*-acetyl derivative would require C = 44.03; H = 4.58 per cent.

This substance is remarkably stable as compared with the compounds of the acid hitherto studied, since it may be boiled with water without change. It is insoluble, or nearly so, in cold water, but dissolves easily in hot water, from which it separates, on cooling, in beautiful, long, glistening, oblique prisms. Ether, alcohol, and glacial acetic acid all dissolve it easily.

Treated with ferric chloride and alkali, it gives no colour, but, after saponification with aqueous potash, it gives the fine violet coloration with ferric chloride characteristic of the original acid.

Strong aqueous ammonia dissolves it after a few minutes, forming a deep orange coloured liquid.

Action of Acetyl Chloride on the Original Acid.

About 2.5 grams of the original dry acid were mixed with about 20 grams of acetyl chloride, and heated on a water bath in a reflux apparatus for about an hour. After expelling the excess of acetyl chloride by heat, the clear liquid solidified, on cooling, to a mass of large, transparent crystals; these were left in a vacuum desiccator over solid potash and sulphuric acid for 24 hours, well washed with cold water, pressed in filter-paper, washed two or three times with anhydrous ether, and finally recrystallised from anhydrous ether, and dried in a vacuum desiccator.

0.1853 gave 0.3044 CO₂ and 0.0464 H₂O. C = 44.80; H = 2.78.

This result coincides almost exactly with that required for a di-

acetyl anhydride, or $O < \begin{array}{c} \text{CO} \cdot \text{CO} \cdot \text{COCH}_3 \\ \text{CO} \cdot \text{CO} \cdot \text{COCH}_3 \end{array}$, namely, C = 44.85; H = 2.80.

A monacetyl anhydride would require C = 41.86; H = 2.32 p. c.

The substance crystallised from ether in minute, hexagonal plates, melting at 98°, and orthorhombic in symmetry. It is somewhat sparingly soluble in ether, more easily in alcohol or in glacial acetic acid, and only very slightly in cold water, but dissolves more readily in hot water, and the solution, when left in a desiccator, gives a syrupy acid, which will not crystallise.

The aqueous solution gives a fine violet coloration with ferric chloride alone, whereas all the compounds of this acid hitherto studied, only give this colour with ferric chloride in presence of caustic alkali.

On saponification with potash, this substance behaves approximately as a tetrabasic acid, but the results are slightly high, probably owing to the unstable character of the resulting potassium salt of the original acid. Thus, 0.3738 gram of substance was mixed with 50 c.c. of alcoholic potassium containing 0.01407 gram KOH per c.c. After shaking and standing for some time, water was added, and the mixture was titrated with N/10 H₂SO₄, of which 50.7 c.c. were required for neutralisation. 29.8 c.c. of the alkali were, therefore, neutralised by the anhydride; theory requiring 27.5 c.c.

Action of Benzoyl Chloride on the Original Acid.

The original dried acid was mixed with a considerable excess of benzoyl chloride, and gently heated on a sand bath in a reflux apparatus; after about half an hour, hydrogen chloride ceased to be evolved, and the whole had dissolved to a clear liquid. A mass of transparent crystals separated on cooling; these were washed with a little benzoyl chloride, drained by means of the pump, washed several times with small quantities of ether, dried, and recrystallised twice from hot benzene. A silky mass of short needles (seen under the microscope to consist of very slender, rhombic prisms) was thus obtained, melting at 167—168°. The substance appears to be quite insoluble in water even on boiling; it is, however, easily soluble in warm alcohol, ether, or benzene. Treated with ferric chloride and caustic alkali, it gives the characteristic violet coloration after standing for a few minutes.

0.1266 gave 0.2957 CO₂ and 0.0345 H₂O. C = 63.70; H = 3.02.

Theory for a dibenzoyl anhydride, $O < \begin{array}{c} \text{CO} \cdot \text{CO} \cdot \text{COC}_6\text{H}_5 \\ \text{CO} \cdot \text{CO} \cdot \text{COC}_6\text{H}_5 \end{array}$, C = 63.90;
H = 2.95 per cent.

A monobenzoyl anhydride would require $C = 56.41$; $H = 2.56$ p. c.

Action of Acetic Anhydride on the Original Acid.

The dry acid was mixed with a considerable excess of acetic anhydride, and heated on a steam bath; the whole dissolved after about half an hour, and the heating was continued for about three hours. Most of the excess of acetic anhydride was then removed by evaporation, and the remaining liquid began partly to crystallise on cooling; on adding cold water, a white, crystalline substance separated. This was drained, repeatedly washed with cold water, then with small quantities of ether, and finally recrystallised from ether. It melted at $97-98^{\circ}$, and was in all respects similar to the product obtained with acetyl chloride, the crystalline forms were identical, and it behaved towards solvents and towards ferric chloride in exactly the same way. The specimen prepared in this way gave, on analysis, the following results.

0.1176 gave 0.1942 CO_2 and 0.0304 H_2O . $C = 45.03$; $H = 2.87$.

Action of Aniline on the Original Acid.

The acid aniline salt was prepared by mixing alcoholic solutions of aniline and the original crystallised acid, in the proportion of 1 mol. of aniline to rather more than 1 mol. of acid; the white, crystalline precipitate produced was collected and drained by means of the pump, well washed with alcohol, and dried in a vacuum desiccator.

0.1663 gave 0.3038 CO_2 and 0.0747 H_2O . $C = 49.82$; $H = 4.99$.

0.1566 „ 8.3 c.c. nitrogen at 23° and 742.4. $N = 5.99$.

$C_4H_4O_6 \cdot NH_2 \cdot C_6H_5$ requires $C = 49.79$; $H = 4.56$; $N = 5.80$ per cent.

This salt melts suddenly, and decomposes at 138.5° . With ferric chloride and alkali, it gives the characteristic violet coloration after standing. It is very sparingly soluble in cold water, more easily in warm water. The solution is acid to indicators. The cold aqueous solution is perfectly clear and colourless when first prepared, but on standing for a few minutes it begins to cloud, and gradually deposits a buff-yellow precipitate, this decomposition taking place very quickly if the solution is boiled; the solid salt also turns brown after keeping for a few weeks. The yellow decomposition product is insoluble in cold dilute hydrochloric acid. It dissolves easily in alcohol, ether, and light petroleum, being first darkened in colour, but it could not be obtained in a crystalline form from its solutions. It was analysed in its original state in order to form some idea of its nature, and gave $C = 73.91$, $H = 6.43$, $N = 10.48$. [A dianil of the formula $C_4H_4O_6 + 2C_6H_5 \cdot NH_2 - 4H_2O$ would require $C = 73.2$, $H = 3.8$, $N = 10.6$

per cent.] From this result, and from the change of colour when solvents are added, it is probable that the substance is a mixture.

The *normal aniline salt* was prepared in a similar manner by mixing the substances in the proportion of 1 mol. of acid to rather more than 2 mols. of aniline. The amorphous precipitate produced was drained, washed with alcohol, and dried in a vacuum as before.

0.1680 gave 0.3556 CO_2 and 0.0840 H_2O . $\text{C} = 57.72$; $\text{H} = 5.55$.

0.1556 „ 11.8 c.c. nitrogen at 21° and 751.2. $\text{N} = 8.73$.

$\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{NH}_2 \cdot \text{C}_6\text{H}_5$ requires $\text{C} = 57.48$; $\text{H} = 5.38$; $\text{N} = 8.38$ per cent.

This salt melts and decomposes at $140\text{--}141^\circ$. It slowly gives the violet coloration with ferric chloride and alkali.

It dissolves with great difficulty in cold water, rather more easily in warm water, and the aqueous solution behaves like that of the acid salt, giving a yellow precipitate immediately on boiling, or after a few minutes on standing in the cold. The *solid* salt, however, appears to be more stable than the acid salt, since it becomes very little discoloured, even after keeping for some months.

Action of Hydrogen Bromide on the Original Acid.

(1) Several experiments were made with *water* as a solvent. The dry acid was treated with considerable excess of an aqueous solution of hydrogen bromide saturated at 0° ; the mixture was allowed to stand for several days, and was heated for periods varying from 2 to 36 hours at temperatures from $50\text{--}105^\circ$. In no case was a very satisfactory result obtained, since either the acid remained apparently unchanged,* or decomposition occurred with production of tarry matter and evolution of carbon dioxide.

(2) Glacial *acetic acid* was next tried, the dry substance being mixed with about 10—30 times its volumes of glacial acid, and the mixture saturated with dry hydrogen bromide at $0\text{--}15^\circ$. The results obtained were of much interest and will be described below (p. 558).

(3) Using *anhydrous ether* as a solvent, a somewhat unexpected result was obtained. The dry acid was mixed with about 30 times its volume of anhydrous ether, and the mixture saturated, or nearly saturated, with dry hydrogen bromide, an operation requiring about six or seven hours for completion.

The original dry acid is very sparingly soluble in ether, but a larger proportion dissolves as the liquid becomes saturated with hydrogen bromide, and, after standing for a day or two with occasional shaking, the whole dissolves forming a clear liquid. [In some

* Later experiments have shown that if the mixture is kept at the ordinary temperature for several days, the acid is transformed into the β -modification (*vide supra*).

cases a heavy oily layer separated, which disappeared on shaking and standing. This may have been the compound of ether with hydrogen bromide observed by Messenger and Engels (*Ber.*, 1888, **21**, 327).]

After concentrating the liquid to about quarter of its bulk by distilling under reduced pressure, and leaving it for a short time, the whole becomes nearly solid, owing to the formation of a mass of fine, long transparent needles or prisms. These were drained with the aid of the filter pump, washed with a few drops of ether, and recrystallised from ether. The substance contained no bromine.

0.1261 gave 0.2140 CO_2 and 0.0674 H_2O . $\text{C} = 46.28$; $\text{H} = 5.93$.

In order to ascertain whether the change had been complete, the same specimen was re-dissolved in ether, saturated again with hydrogen bromide, and the crystals separated and recrystallised as before. These crystals melted at $74-75^\circ$. The substance gave the following result on analysis.

0.1110 gave 0.1900 CO_2 and 0.0596 H_2O . $\text{C} = 46.68$; $\text{H} = 5.96$.

A substance formed by replacing two atoms of hydrogen in the original acid by ethyl, $\text{C}_4\text{H}_2(\text{C}_2\text{H}_5)_2\text{O}_6$, would require $\text{C} = 47.05$ and $\text{H} = 5.88$ per cent.

This product may, therefore, be either the diethyl derivative of the acid, or the diethylic salt. It has, however, no acid properties, its solution in aqueous alcohol being neutral to litmus, and giving no effervescence with sodium carbonate; moreover, it proves to be absolutely identical with the product described below. One may, therefore, conclude that this substance is the *diethylic salt* of the acid.

The ether used in the foregoing operations was most carefully purified from alcohol and from water. It was washed four or five times with small quantities of water, digested for a fortnight with a large excess of calcium chloride, and afterwards boiled for four hours in a reflux apparatus with sodium wire; it was then distilled with every precaution to prevent access of moisture. The hydrogen bromide employed was dried first with calcium chloride and then with phosphorus pentoxide.

I am not aware that the formation of ethylic salts in this manner has been observed before. It is possible that the method might be of advantage in certain cases, and I hope to make experiments in this direction with other acids. [A similar result could not be obtained by substituting hydrogen chloride for hydrogen bromide. Ethylic bromide appears to have no action on the acid, even after several hours heating in a sealed tube.]

Further evidence that the substance is the diethylic salt is afforded by the fact that a product identical with it in every respect is obtained by the ordinary method of preparing ethylic salts. Dry hydrogen

chloride was passed to saturation into a solution of the anhydrous acid in ethylic alcohol; it is advisable to use considerable excess of alcohol (about 1 part acid to 20 parts alcohol), and to allow the mixture to become warm, otherwise some of the acid may separate out unchanged. The mixture was allowed to stand for 24 hours, and then concentrated by distillation under reduced pressure to about one-fourth of its bulk. On standing for a short time, a mass of transparent needles separated exactly as in the experiment last described; these, on recrystallisation from anhydrous ether, melted at $72-73^{\circ}$, and were identical in crystalline form and all other properties with the product obtained from ether and hydrogen bromide.

0.1398 gave 0.2404 CO_2 and 0.0745 H_2O . $\text{C} = 46.89$; $\text{H} = 5.92$.

$\text{C}_4\text{H}_2(\text{C}_2\text{H}_5)_2\text{O}_6$ requires $\text{C} = 47.05$; $\text{H} = 5.88$ per cent.

In both of these methods of preparation, a further yield of the ethereal salt may be obtained by adding water to the supernatant liquid after draining off the crystals.

This substance, prepared by either method, exhibits the following remarkable property. It is quite stable when exposed to the atmosphere at ordinary temperatures. Specimens have been kept exposed for months without change. If, however, it be placed in a desiccator over sulphuric acid, phosphorus pentoxide, or caustic potash, it begins to *liquefy* after a few hours, a small quantity (say 0.5 gram) being entirely converted to the liquid state after about 15—24 hours. After remaining in the desiccator for some weeks it again becomes a solid crystalline mass. Examined quantitatively, it is seen that a slight *increase* of weight always takes place at first, and that this is followed by a regular and diminishing *loss*, which continues for several weeks, constancy being apparently attained when the whole has solidified.

If the original crystals of the ethereal salt be sealed up in a tube full of *air*, and containing phosphorus pentoxide, the same change takes place, whilst if *oxygen* be substituted for air the effect is much more rapid. But if the tube be filled with *hydrogen* or *carbon dioxide* instead of air, the crystals remain *permanent*. This phenomenon is still under investigation.

The ethylic salt crystallises in very slender, oblique prisms. It is practically insoluble in water, but dissolves easily in alcohol, and very easily in ether. Treated with ferric chloride and caustic alkali, it gives the characteristic violet coloration after a short time; and with caustic alkalis alone, or with ammonia, it gives a lemon-yellow coloration. Its behaviour with these reagents is exactly similar to that of the methylic salt previously described. With sodium ethoxide, its alcoholic solution gives a bright scarlet precipitate which is extremely unstable, and soon turns yellow, and then colourless. So far, it has not been found possible to analyse this owing to its instability.

The action of the *chlorides of phosphorus* has been only partially studied, since the results so far obtained from them give no very definite information concerning the subject under investigation, but their behaviour will be discussed in a future communication.

Constitution of the Acid.

The molecular weight of the acid has been determined by a vapour-pressure method and by the boiling-point method, and that of the methylic salt by the freezing-point method. It is further confirmed by the direct relationship to tartaric, succinic, and dihydroxytartaric acids, and by its simple resolution into glycollic aldehyde and carbon dioxide.

The *di-basicity* of the acid has been established by titration with alkali and by analysis of the ammonium, sodium, methyl and ethyl salts, and of the normal and acid aniline salts.

The presence of *two hydroxyl groups* has been shown by the action of acetyl chloride on the methylic salt, and that of acetyl and of benzoyl chlorides and of acetic anhydride on the free acid, di-acidyl derivatives, which withstand the action of water, being obtained in each case.

The *absence of a ketonic group* is indicated by the negative behaviour of phenylhydrazine and of hydroxylamine towards the methylic and ethylic salts. The crystalline compounds obtained when these agents react with the free acid are shown to be the normal phenylhydrazine and hydroxylamine salts respectively.

Direct evidence of the *unsaturated* nature of the acid is not easy to obtain, owing to the unstable character of many of the additive products. It is indicated, however, in the production of tartaric (or racemic) acid by the limited action of hydrogen iodide, and in the fact that it instantly decolorises alkaline potassium permanganate (Baeyer's test).

Many of the transformations can be readily understood if the formation of unstable intermediate additive products be assumed. Bromine, for example, appears to be without action on the dry acid, but it is immediately decolorised by the hydrated acid, the change being complete if a small quantity of water be added. The result is dihydroxytartaric (tetrahydroxysuccinic) acid and hydrogen bromide. This change is readily explained if it be assumed that the unstable additive product, $C_2Br_2(OH)_2(COOH)_2$ (dibromotartaric acid), is first produced and then hydrolysed. The fact that water is essential for the splitting up of the acid into glycollic aldehyde and carbon dioxide, may be explained in a somewhat similar manner (*loc. cit.*, 774).

The colour reactions with ferric chloride (green in presence of

mineral acid, changed to violet by alkali) remind one of the "pyrocatechin reaction" characteristic of orthodihydroxy-derivatives. This fact might, perhaps, be suggested as further evidence in favour of the dihydroxylic formula.

Taking all the above stated facts into consideration, it is evident

that the original acid must be represented by the formula

$$\begin{array}{c} \text{COOH} \\ | \\ \text{C} \cdot \text{OH} \\ | \\ \text{C} \cdot \text{OH} \\ | \\ \text{COOH} \end{array},$$

and that it is, therefore, either *dihydroxyfumaric acid* or *dihydroxymaleïc acid*.

The readiness with which anhydrides are produced by the actions of acetyl or benzoyl chlorides, and of acetic anhydride, affords suggestive, although not conclusive, evidence in favour of the maleinoid constitution. More direct information is supplied by the behaviour of the aniline salts. Gottlieb, Perkin, Michael, and others have shown that the aniline salts of maleïc, citraconic, and allied acids are very unstable as compared with those of the fumaric series (fumaric, mesaconic, &c.). The former readily lose water, giving anilides, or anils, or isomers of these or mixtures, when solutions of the salts are heated or allowed to stand. Michael recommends that the acid should be half neutralised with aniline, and the solution allowed to stand or boiled, when acids of the maleïc series give precipitates (insoluble in dilute hydrochloric acid), whereas those of the fumaric series are stable. By reference to the properties of the aniline salts mentioned above, it will be seen that the acid under discussion behaves as a member of the *maleïc* series.*

Isomeric or Modified Form of the Acid.

The original acid is very sparingly soluble in cold glacial acetic acid. It dissolves fairly easily on heating, but the greater part

* Experiments are being made with a view of producing the acid, or its derivatives, from other sources, *e.g.*, from acetylenedicarboxylic acid, tribromosuccinic acid or dibromomaleïc acid.

Bourgoin, in 1874, stated (*Bull. Soc. Chim.*, **22**, 443) that by the action of water on silver dibromomaleate he had obtained an acid having the formula $\text{C}_4\text{H}_4\text{O}_6$, and which he called "dioxymaleïc acid." He gave, however, no experiments in support of this statement, with the exception of a single silver determination, the result of which was, of course, capable of other interpretations. His conclusion was afterwards called in question by Scherks (*Annalen*, 1881, **207**, 223), and the experiment was repeated by Hendrixson (*Amer. Chem. J.*, 1890, **12**, 325), who obtained only acetic acid and carbon dioxide.

Tanatar (*Ber.*, 1879, **12**, 2293), by the action of potassium permanganate on fumaric acid, obtained a substance to which he assigned the formula $\text{C}_4\text{H}_4\text{O}_6$, and which he called "bioxyfumarsäure," but which was subsequently shown to be racemic acid.

separates out again on cooling, and if the remaining solution be evaporated to dryness, the anhydrous acid remains as a white, amorphous powder which, as previously shown, is only slightly soluble in water or ether. If, however, the dry acid be covered with glacial acetic acid and dry hydrogen bromide passed to saturation, the mixture being kept cool, a very different result is obtained; under these circumstances a much larger proportion of the acid dissolves, and if the mixture be afterwards heated until solution is complete, no separation occurs on cooling. Although heating considerably hastens the process, it is not necessary to bring about the change, since the whole dissolves after standing for a few days and shaking. The following is the method usually adopted: About 5 or 6 grams of the dried acid is mixed with excess (about 30 times its volume) of glacial acetic acid, and thoroughly saturated with dry hydrogen bromide, the mixture being cooled by ice towards the end of the operation; it is allowed to stand for a day or two, and then heated in a pressure bottle at about 60—80° for a few hours.* After again standing for a day or so, it is advisable to saturate the mixture once more with hydrogen bromide.

On evaporating to dryness a few drops of the resulting liquid, a brilliant, crystalline residue is left, which is extremely easily soluble in water and in ether. It is highly deliquescent, the crystals immediately becoming liquid if breathed upon, or if subjected to the vapour of ether.

On removing the hydrogen bromide and the greater part of the acetic acid by distillation under reduced pressure, a liquid remains, which sets to a crystalline mass on cooling (Product A). A little of the original acid usually remains unchanged, and, in order to remove this, the product is extracted with ether, distilled nearly to dryness, and the resulting crystals extracted with glacial acetic acid; or the product may be mixed with a little water, extracted with ether, the ethereal solution dried over calcium chloride or anhydrous sodium sulphate, and distilled to a small bulk. The solution from either of these operations, on standing in a desiccator, soon deposits a mass of transparent prisms; these are very easily soluble in water or ether, and fairly easily in cold glacial acetic acid. They rapidly deliquesce when exposed to the air, and give off acetic acid. When heated, or placed in a desiccator over potash, they quickly effloresce, giving off acetic acid, and leaving a white residue (Product B). This residue is also extremely deliquescent, and easily soluble in water and in ether, separating from its solution in ether as a mass of radiating, feathery crystals.

* This is a somewhat dangerous operation, as explosions sometimes occur, but little harm results if the heating be effected in a sufficient volume of water.

When either of these products, A or B, is dissolved in water, a perfectly clear solution is obtained, but, on allowing the solution to remain for some hours, preferably in a vacuum desiccator, it begins to deposit short, rod-like prisms, or long, silky, prismatic needles, very sparingly soluble in cold water (Product C).

Examination of Product A.—The crystals were drained, washed quickly with a little glacial acetic acid, and pressed for some time in dry filter-paper. Owing to their extreme deliquescence and instability, much care was necessary in order to avoid exposure to the air.

I. 0.1484 gave 0.2044 CO_2 and 0.0521 H_2O . $\text{C} = 37.56$; $\text{H} = 3.90$.

II. Another specimen was washed as before, and very quickly pressed between two or three changes of dry filter-paper.

0.1910 gave 0.2663 CO_2 and 0.0663 H_2O . $\text{C} = 38.02$; $\text{H} = 3.85$.

These numbers approximately indicate the formula $\text{C}_4\text{H}_4\text{O}_6 + 2\text{CH}_3\cdot\text{COOH} - \text{H}_2\text{O} = \text{C}_8\text{H}_{10}\text{O}_9$, which requires $\text{C} = 38.40$; $\text{H} = 4.00$ per cent.

III. Another specimen was heated in an air bath at 95° till the weight was constant.

0.2282 lost 0.1115 = 48.86 per cent.

IV. A further specimen was heated in a current of dry hydrogen, the loss of weight was estimated, and the acetic acid evolved was determined by absorption in normal potassium hydroxide.

0.2429 lost 0.1170 = 48.16 per cent.

Theory for a loss of $2\text{CH}_3\cdot\text{COOH}$ from $\text{C}_8\text{H}_{10}\text{O}_9 = 48.00$ per cent.

The resulting acetic acid neutralised 1.9 c.c. normal $\text{KOH} = 0.1140$ gram of acetic acid. Theory = 0.1165 gram.

Examination of Product B.—The residue from Analysis III was somewhat discoloured, and was, perhaps, somewhat affected by the air, as is the case with the original acid.

V. 0.1516 gave 0.2014 CO_2 and 0.0214 H_2O . $\text{C} = 36.23$; $\text{H} = 1.56$.

VI. The residue from IV was nearly pure white, and gave the following result.

0.1259 gave 0.1702 CO_2 and 0.0183 H_2O . $\text{C} = 36.86$; $\text{H} = 1.61$.

The formula $\text{C}_4\text{H}_4\text{O}_6 - \text{H}_2\text{O} = \text{C}_4\text{H}_2\text{O}_5$ requires $\text{C} = 36.91$; $\text{H} = 1.53$ per cent.

This substance gives the characteristic violet coloration when treated with ferric chloride and caustic alkali. With alkalis alone, and with ammonia, it gives a deep yellow coloration, and with barium hydroxide, a bright yellow precipitate is produced. Towards *sodium carbonate*, it behaves as a monobasic acid, using methyl-orange as indicator. Thus.

VII. 0.1394 substance required 11 c.c. $\text{N}/10 \text{Na}_2\text{CO}_3$ for neutralisation.

VIII. 0.1568 substance required 11.8 c.c. N/10 Na_2CO_3 for neutralisation.

Theory for a monobasic acid = 10.7 c.c. and 12.0 c.c. respectively.

With caustic alkalis, the results are much higher, 0.1752 required 22 c.c. N/10 KOH.

Theory for a monobasic acid = 13.4 c.c.

Examination of Product C.—The air-dried crystals gave the following results.

IX. 0.1395 gave 0.1317 CO_2 and 0.0537 H_2O . C = 25.74; H = 4.27.

X. 0.1318 „ 0.1247 „ 0.0501 „ C = 25.80; H = 4.29.

The formula $\text{C}_4\text{H}_4\text{O}_6, 2\text{H}_2\text{O}$ requires C = 26.08; H = 4.02 per cent.

XI. Another specimen was heated at 80–85° in a current of hydrogen until the weight was constant.

0.2456 lost 0.0481. H_2O = 19.58.

Theory for a loss of $2\text{H}_2\text{O}$ from $\text{C}_4\text{H}_8\text{O}_6$ = 19.56 per cent.

These results are identical with those obtained on analysis of the original acid. (For the sake of reference, we will call the original acid the α -modification, and the Product C the β -modification.)

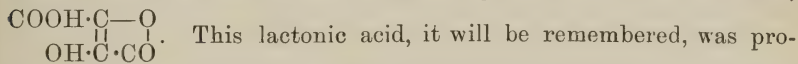
The properties of the two are in many respects identical or very similar. Both give the characteristic violet coloration with ferric chloride and alkali, the behaviour on heating is much the same, and the solubilities appear to be almost identical, about 5 parts per 1000 at 15°. The accuracy of the solubility determinations cannot, however, be depended on, owing to the unstable character of the aqueous solutions which decompose spontaneously even at low temperatures. The crystalline forms and the appearance are, however, altogether different, the α -acid crystallising in diamond-shaped plates, and the β -acid in prisms or needles. Both acids lose their water of crystallisation on heating, leaving white, amorphous powders, and, on dissolving these in small quantities of hot water, each crystallises out again in its original form, that is, the α -acid in diamond-shaped plates, and the β -acid in prisms.

The acid aniline salt of the β -acid appears to be much more stable than that of the α -acid, and the difference is very striking if the experiments are made side by side. Weighed quantities of the respective acids are dissolved in alcohol, and aniline is added in alcoholic solution in quantity calculated for the acid salt (1 mol. acid to 1 mol. aniline). The precipitates obtained are collected, washed with alcohol, and thoroughly drained with the aid of the pump; they are then ground up with small quantities of cold water, filtered, and the filtrate heated gradually to boiling under the same conditions. The salt of the α -acid, as previously shown, very soon begins to cloud, and eventually deposits a buff-yellow precipitate, whereas the salt of the β -acid remains perfectly clear for a considerable time. It is true that some

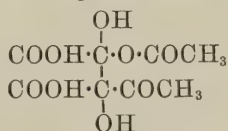
specimens of the aniline salt of the β -acid also showed a cloudiness after a time, but the difference from the α -salt, even then, is very easily seen. This slight clouding of the solution of the β -salt is probably due to the fact that it is very difficult to obtain specimens of β -acid entirely free from traces of the α -acid; examined under the microscope, one or two diamond-shaped crystals are sometimes found mixed with the prisms or needles. This circumstance may be due to the fact that the methods of purification are not perfect, or to a partial change back to the original form.

From the foregoing observations it seems evident that the difference between the α - and β -acids is more than a mere crystallographic one, and, considering the mode of formation of the β -acid, and the relative stability of its acid aniline salt, it appears not improbable that it represents the fumaroid form, *i.e.*, that it is dihydroxyfumaric acid. The formation of this acid from the corresponding maleinoid form could be explained by the Van't Hoff-Wislicenus hypothesis in a manner similar to that which accounts for the transformation of maleic into fumaric acid by the action of hydrogen bromide. The intermediate product might, for example, be tribromosuccinic acid* or trihydroxysuccinic acid, which could lose hydrogen bromide or water, giving a fumaroid derivative. Referring, however, to the two intermediate products which were isolated from the acetic acid hydrogen bromide reaction mentioned above, the following explanation may be suggested.

The Product B, having the formula $C_4H_2O_5$, might be the anhydride, "internal ether," or lactonic acid, but, from its behaviour with sodium carbonate and with alkalis, and from the fact that its aqueous solution, on standing, readily yields the β -acid, there seems to be little doubt that it is the *lactonic acid*, having the fumaroid constitution,

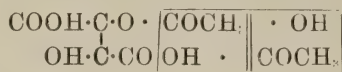


This lactonic acid, it will be remembered, was produced by heating the crystalline Product A, 2 mols. of acetic acid being given off at the same time. The acetic acid might be present as "acetic acid of crystallisation," but it seems more probable that the Product A is a compound formed by the addition of the elements of acetic anhydride to the original unsaturated dihydroxymaleic acid,

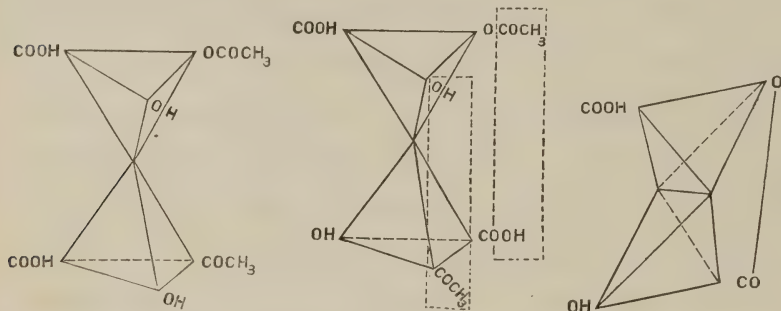


* When the original acid is heated with amorphous phosphorus and bromine, a product is obtained which, on being dissolved in water, deposits crystals after a time, apparently identical with the β -acid, and a similar effect is slowly produced by aqueous hydrogen bromide.

This product might then, after "rotation," lose $2\text{CH}_3\cdot\text{COOH}$ in the following way.



leaving the lactonic acid.



This explanation is, of course, only offered as a suggestion.

I hope shortly to make further observations on this β -acid, and also on the lactonic acid which appears to have some remarkable properties. The side-issues of the present work have, however, revealed so many interesting fields for investigation, that it is somewhat difficult to decide which should next be taken in hand.

University Laboratory, Cambridge,
March 17th, 1896.

ANNUAL GENERAL MEETING,

March 26, 1896.

Mr. VERNON HARCOURT, President, in the Chair.

THIRTY-ONE years ago I had the honour of being elected Secretary of the Chemical Society. We used then to meet on the ground-floor of the original Burlington House, which the artists now occupy, on the east side of the entrance, and it was during my eight years of office that the present home of the learned societies was built, and that we moved into the rooms in which we now meet. The collection of specimens presented to the Society, which it was thought in our early days would gradually furnish a chemical museum, was dispersed at the time of our removal, the decision having to be made whether we should appropriate a room and shelves to such a museum or not. Mr. John Williams put a modest price upon the articles, at which they were taken by various members of the Council. No doubt the decision was right. It requires an effort of the imagination to invest such specimens with a real individuality. Among my share was a small bottle of the beautiful, silky-red needles of chromic acid, now trioxide, prepared and presented by our founder, Mr. Warington. But the substance had become common, and one needed, in order to feel interest in the specimen, to rest upon the historical evidence that those were the actual crystals Mr. Warington had prepared. Another specimen I remember of native mercury from Idria. For many years it was religiously kept apart, but at last some laboratory boy, unconscious of the difference between it and other mercury, added it to the general stock. Many other specimens had succumbed to the property of slow chemical change, a property existing, no doubt, in a number of substances which, in our hurried way, we deal with before the year is out, and are not content to watch. It might by now have been of great interest to examine some of the decomposed specimens of this miscellaneous collection.

We decided against the museum, but arranged for a room adjoining our meeting room, which should be fitted up as a laboratory, and provided with such ordinary apparatus and materials as might help, and so encourage, authors to illustrate their communications experimentally. I fear this plan has failed, like that of a museum. Figures and formulæ, and drawings on the blackboard, form the chief part of what chemists now have to show to one another. But I observe that

the old love for an experiment, though it may have been most keen in the boyhood of our science, as in the boyhood of each one of us, still remains. When the liquefaction of air in a cooled test-tube is to be shown, or the phosphorescence of the platinocyanides under the penetrating influence of the Röntgen rays, we have even larger meetings than usual, and a still more interested audience. The feelings with which we first saw solid carbon dioxide, or evidence of the extension of the spectrum beyond the visible limits of red and violet, or the action of the screened off magnet, are re-awakened. In view of this fact, those who contribute to our proceedings should bear in mind that anything they may have to show will meet with a welcome sufficient to reward them for the trouble which the bringing and setting up of apparatus involves. It is not only such wonderful scientific discoveries as those to which I have referred, which should be illustrated here. We have been glad to see the simple production of acetylene, from some lumps of calcium carbide in a bottle, and some water in a dropping tube, the brilliant light which the gas gives, and the flame of its decomposition in a heated tube. We are also indebted to Professor Lewes for showing before us that cyanogen mixing with nitric oxide burns like a hydrocarbon. Further, novelty in apparatus is worth showing, even a new dephlegmator or nitrometer. In a few minutes, with a few words of description, every one can judge whether the apparatus shown is in any respects better than that which he is accustomed to use; and many a useful hint, or the germs of further improvements, may thus be imparted.

I have referred to experiments on acetylene, and this recalls the evenings we have spent in listening to a discussion of the nature of hydrocarbon flames, their temperature in different regions, and the causes of their luminosity. The attractive phenomenon of flame no longer holds the place it once held in chemical theory; but at long intervals, on two or three occasions, a discussion has arisen regarding what may be called the topography of flames. Indeed, the delimitation of the zones, and the estimation of the temperature and material constitution of portions of the flame, are so difficult that we cannot yet with confidence give a complete account of that which happens in any single flame. Before one of our recent discussions, I was asked by a friend to conclude the proceedings with a judicial summing up, and to declare which disputant was in the right. I declined to undertake the task. I do not underestimate the dignity, for which I am grateful to you, of occupying this chair; but it does not entitle, and certainly does not qualify, its holder to pronounce *ex cathedra* on any subject as to which a difference of opinion exists between honest and capable investigators. Taking, however, the humbler position of a jurymen, I should have supported a verdict to this effect,

that it was highly probable (which our law calls "proved") that the splendour of the flame of acetylene is due to, among other things, the high temperature caused by the addition of its heat of decomposition to its heat of combustion; but that it was not proved that the brightness of an ordinary flame of coal-gas was due in any degree to the formation and subsequent combustion of acetylene.

At our anniversary meeting last year the usual proceedings were suspended for a short time, that we might hear from Professor Ramsay an announcement of unusual interest. The President, in delivering the Faraday Medal to Lord Rayleigh, had congratulated him on the wonderful discovery of a new constituent of the atmosphere, which had sprung from his careful determination of the density of nitrogen, and in the working out of which he and Professor Ramsay had borne an equal share. The announcement which Professor Ramsay had then to make to us was of the discovery of another similar substance, of which he has since given a further account. Among many points of interest attaching to helium one of the strangest is this, that being what it is, there should be any of it on earth. It has been happily named, for the sun would seem to be its natural resting place. Assuming the correctness of Dr. Johnstone Stoney's calculations, hydrogen once set free, if it escapes a flash of lightning, passes out into space beyond the limits of our atmosphere. But hydrogen does not readily get free; it may pass from its combination with oxygen into complex organic molecules, and issue thence in combination with carbon or nitrogen or sulphur or phosphorus, and thence become united with oxygen again. Helium has no such ties to retain it. With no element which has been offered to it has it yet been found, at any temperature, to combine. Once set free, it is not even absorbed again by the materials which held it.

In glancing back at the chemical events of the past year, to which many of our Fellows have contributed, we must, I think, wish to accord our heartiest congratulations to Professor Ramsay on his great good fortune in happening upon these wonderful substances, and on the skill and insight with which he has investigated them.

Many of the papers brought before us have been of great interest; some standing alone, others the periodical record of long and systematic work. On every occasion the readers of papers have found an interested and appreciative audience.

A difficulty, however, arises at our meetings owing to the large number of communications we receive. When we have sat from 8 to 10, we feel we have had a full meal and are inclined to rise from table. Yet it often happens that we have only gone through half the papers on our list. I see no better way out of this difficulty than that of judging on each occasion, on various grounds, in what

order papers should be taken. One obvious ground is to accord a preference to the papers which come first into the Secretaries' hands ; another, to give a preference to those papers whose authors are present, and especially if they have arranged any experimental illustrations. Again, some papers are more likely than others to give rise to an interesting discussion ; and our chief reason for meeting, is not that we may hear instead of reading,—often reading is better,—but that we may ask questions and discuss, or listen to questions and discussions. I think that as far as possible every author should be asked whether if there is not time for the reading of his paper, he had rather that it should pass at once into the hands of the Publication Committee, or that it should be reserved for another meeting. A list might also be posted up in the Library, as has been suggested by a member of Council, of all papers received, so that anyone who went to the Library might judge whether the occasion was favourable for sending in his paper. These, however, are matters for the judgment of Council, and especially of the Secretaries.

From our Senior Secretary I have obtained some notes of the Proceedings of Council during the past year, to which I will now briefly refer.

On the recommendation of the Treasurer, who bestows on the affairs of the Society an amount of care and financial ability of which only members of Council can be fully aware, the fees for composition have been put on a proper basis.

We have twice been in communication with our French neighbours and colleagues, once on the sad occasion of M. Pasteur's death, and again on the celebration of the hundredth anniversary of the *Institut*.

The Council having determined to publish a Collective Index of the publications from 1873 to 1892, in two volumes, decided to send copies of both volumes to those who have been Fellows since the end of 1882, and the second volume only to Fellows who have joined the Society between the 1st of January, 1883, and the 31st of December, 1892.

On the question of indexing, which has been also occupying the attention of the Royal Society, a Committee of the Council has been appointed, and will, I believe recommend the continuous preparation of a subject index to our Transactions, Proceedings, and Abstracts.

Shortly before our meeting at the end of last year, at which a number of candidates were elected, a printed list of candidates was sent round unofficially and anonymously, on which the attention of the Fellows was called to certain candidates, obviously with the intention that they should be black-balled. The matter came before the Council, and as their feeling was strongly adverse to the issue of

such anonymous appeals, I was asked to mention it to the Society. Our objection is not to the unofficial character of this circular, though it is clear that the Fellow or body of Fellows who issue such an appeal undertake a considerable responsibility, and should make clear on the face of their circular that it is unofficial. But we think that those who issue the circular should append their names. The fact that our voting is by ballot does not, we think, justify the circulation of an anonymous attack upon some of the candidates.

At our last anniversary meeting reference was made to the long delay which has occurred in printing an account of the proceedings at the jubilee of the Society. The principal cause of this delay appears to have been a sort of heroic error on the part of my predecessor in this chair. Probably no occupant of the chair has ever done so much work for the Chemical Society. Dr. Armstrong undertook to write, as a supplement to the jubilee narrative, an account of the scientific work of our Society during the first 50 years of its existence. As he advanced down the rapidly swelling stream of chemical inquiry the task became more and more arduous, while his leisure was invaded by the growing claims of other work, including the Presidency of this Society. At length, however, the difficulties which had thus arisen have been faced and overcome. The record of the jubilee will, it is hoped, consist of two volumes. The first is all but complete; indeed, it was hoped that copies might have been issued in time for this meeting. It contains a report of the speeches made at the jubilee meeting and at the dinner which followed, and an account of the early history and development of the Society.

The second volume, which Dr. Armstrong tells me he has nearly completed, will contain the record of our work from the foundation to the jubilee.

We have also another arrear as to which we can now make a similar announcement. The addresses delivered at the Hofmann Memorial Meeting, which have been prepared for publication by my predecessor, who is also contributing some account of Dr. Hofmann's work, will, we are informed, be ready to appear in an early number of the Journal.

We have listened, so recently that a slight reference will suffice, to a memorial lecture on the work of one of our most distinguished foreign members, Professor von Helmholtz. Early in the century there were men who made science their subject. They listened to and read omnivorously all that came before the Royal Society or the British Association. Such a man I knew in my uncle, W. Vernon Harcourt, a Fellow of this Society, who was the principal founder of the British Association; and the correspondence of his scientific contemporaries, which I have been reading, shows that they succeeded

in covering, or at least in interesting themselves in, the whole of the scientific knowledge of their day. But during the last half century that a man should have a full knowledge of many distinct sciences, and should do admirable work in all of them, has been possible only to such a giant as Helmholtz. Professor Fitzgerald gave us in his lecture some criticisms of physical theories, imagined and largely adopted by chemists, which we shall do well to consider. It is possible that we have listened to a false cry, and got on to a wrong scent, all of us together. We are not wiser than our fathers, the adherents of phlogiston, were.

Two of our foreign members have died within the year. Eleven days after our last anniversary occurred the death of Dr. Lothar Meyer, whose work on the modern theories of chemistry, frequently re-edited, has during 30 years made his name widely known. Beginning as a doctor of medicine, he investigated the gases in the blood, and was thus drawn to Chemistry. For the last 20 years he worked and taught as Professor at Tübingen. It is pleasant to read in the sketch of his life given in the *Berichte* that the award by the Royal Society to him, conjointly with Mendelejeff, of the Davy Medal, for his share in the development of the periodic law, gave him especial pleasure. His life and work are to be the subject of a memorial lecture which Professor Bedson has promised to deliver here on the 28th of May.

The second foreign member whom we have lost was M. Pasteur, whose marvellous work in the study, first of crystals and then of micro-organisms, and whose applications of his discoveries to the benefit of mankind, have been recalled since his death on September 28th to the memory of us all. An admirable lecture on the life and work of Pasteur was given to the British Association at Ipswich, shortly before his death, by Dr. Percy Frankland. It is proposed that in the course of this year a memorial lecture, especially on the chemical aspect of Pasteur's work, should be given here.

During the coming summer, celebrations are to be held of the completion of periods in the lives of two distinguished men of science. The Society has been asked to send a representative on the 15th of June next to take part in the celebration of the completion by Lord Kelvin of the fiftieth year of his tenure of the Chair of Natural Philosophy in the University of Glasgow. Our senior Secretary, himself a Glasgow student, has been asked by the Council to represent us on this auspicious occasion. In July next there occurs the seventieth anniversary of the birth of Cannizzaro. An address of congratulation has been drawn up by our Foreign Secretary, which will be presented on his birthday to the illustrious Italian chemist.

A letter was received 10 days ago from the Secretary to the Board

of Trade announcing that they had determined, in consequence of a report on the accident at the St. Neots Station, to appoint a Committee to inquire into the loss of strength in steel rails used on railways, and asking that the Chemical Society would select two members to be submitted to the President of the Board of Trade as suitable members of the Committee. The Council have nominated our Treasurer, Dr. Thorpe, and our junior secretary, Professor W. R. Dunstan, to take part in this interesting and important inquiry.

Of our own ordinary members we have lost 15 by death during the year, namely, the following:—Cave, Herbert; Davy, S. H. M.; Gal-
loway, R.; Kelly, J. A.; Liepmann, Hy.; Linford, J. S.; Looker, P.;
McRoberts, G.; Morgan, Wm.; Offord, J. A.; Pochin, H. D.; Smith,
C. H.; Smith, M. H.; Winstone, A. B.; Wood, John.

The following 24 have resigned:—Ansell, F. G.; Briggs, H. F.;
Cory, G. E.; Gardner, J.; Greenish, T.; Groves, T. B.; Haydon,
W. F.; Heyes, Rev. J. F.; Holt, W.; Jackson, W.; Kay, Rev. W.;
McKillop, J.; McMullan, C.; Pullinger, F.; Maben, T.; Rothwell,
R. R.; Sergeant, E.; Smith, Prof. E. F.; Stocks, J. M.; Truman,
E. B.; Bose, C. M. von; Wethered, E.; ~~Liversidge, Prof.~~; Snelus, G.

The following have been removed by the Council (from our list of
Members on account of non-payment of subscriptions:—) *See errata*
1869-18756

Three years' arrears:—Ashcroft, G. A.; Adams, F. E.; Billing,
H. S.; Burnett, E. E.; Bamber, H. K. G.; Babington, P.; Byrne,
Thos.; Baine, L. A.; Campbell, J. M.; Cook, Rev. E. B.; Cole, A.;
Davies, D. O. S.; Foster, J. A.; King, C. M.; Kirkman, H. J.;
Kacker, K. K.; Lennox, D.; Lintern, A. A.; MacLeroy, A. L.;
Mousley, H. J. M.; North, W.; Quayle, E.; Stephens, C. W.;
Wells, G. I. J.; Wiltshire, John; Evans, A. J.; Phipson, T. L.;
Blyth, F. W. G.

Two years' arrears:—Ainsworth, Geo.; Bamber, W. E.; Chant-
rell, P. S.; Cooper, L.; Chaney, H. J.; Cargill, W. D.; Edmunds,
Lewis; Golden, A. R.; Hope, C. F.; Jenkins, Wallis; Mansell, J.;
Parker, R. H.; Speir, J.; Schlesslman, J.; Tate, Dr. G.; Wilson,
J. M.; Walker, D.

Twenty-four Fellows who have paid a life composition have for
two years not replied to the communications sent them. It is pro-
posed to make another attempt at communicating with them, and if
this fails their names will be removed.

The number of Fellows whose names have been removed is, it will
be seen, unusually large. This is due to the operation of the
amended by-law which was sanctioned at the last meeting. It is
not likely that this change will make the number of Fellows thus
removed larger in the future than in the past. Indeed, we may hope
that a more stringent rule will hinder some of our Fellows from

starting on the downward course of being in arrear. But its immediate effect is that those who would have been next year's defaulters are struck off now.

The present position of the Society in regard to the number of Fellows will be seen from the following tabular statement.

Number of Fellows, March 31st, 1895	1979
" " since admitted	114
" " reinstated by Council	9
	<hr/>
	2102

Removed on account of non-payment of three	
annual subscriptions	28
Do. two annual subscriptions	17
Withdrawn.....	23
Deaths	15
	<hr/>
	83

Number of Fellows, March 31st, 1896	2019
Foreign Members.....	28

The use of the Library, as judged from the issue of books, is on the increase. Last year the number issued was 564; this year it is 675. The number of volumes and pamphlets added to the Library during the past year has been 743.

A shelf-catalogue is in course of preparation to facilitate the checking of the books in the Library; and a new system of registration has been adopted, by means of which it is hoped that the loss of books, taken out but not returned, may be diminished.

The number of papers printed in our Transactions has been 116, and 43 other papers have been printed in the Proceedings only.

The following statistics relating to our Abstracts have been furnished to me by the Sub-Editor.

PART I.

	Pages.	No. of Abstracts.
Organic Chemistry	692	1190

PART II.

General and Physical Chemistry		318
Inorganic Chemistry		234
Mineralogical Chemistry		97
Physiological Chemistry.....		174
Chemistry of Vegetable Physiology and Agriculture		110
Analytical Chemistry		359
	<hr/>	<hr/>
Total in Part II	544	1292
	<hr/>	<hr/>
Total in Parts I and II	1236	2482

The index to the Transactions, Proceedings, and Abstracts occupied 175 pages, of which 120 pages was subject index; 55 pages, index of authors' names.

The grants made to the Research Fund will appear in the Treasurer's Statement. A good return of work done and of communications to the Society is made by those who receive these grants, as may be seen by looking at last year's list. In particular, at our last two meetings we have had communications of great interest and value from Mr. Herbert Jackson and Mr. A. E. Tutton.

The Treasurer will also lay before you, in detail, the financial condition of the Society, which seems to be prosperous, owing largely to his care.

A question of great and increasing difficulty, that of chemical nomenclature, has again been under the consideration of the Publication Committee and of the Council. As this question is partly international, and as a larger number of foreign chemists attend the meetings of the British Association in the summer than our meetings at a busier time of the year, it was suggested that a discussion on chemical nomenclature might be held at one of the meetings of the Chemical Section of the Association. I have no doubt that effect can be given to this suggestion, and I hope that a large number of our Fellows will be able to attend the meeting.

The Obituary Notices will appear in the next monthly part of the Journal.

Dr. GLADSTONE, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed.

Professor DIXON, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having thanked the meeting,

Professor THORPE, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4454; by sale of Journal and advertisements, £511 8s. 3d.; and by dividends on invested capital, £381 15s. 9d. The expenses had been:—On account of the Journal, £2858 10s. 6½d.; on account of the Proceedings, £261 6s. 2½d.; on account of the General Index, £184 2s. 6d.; on account of the Library, £306 17s. 4d.; the total expenditure being £4406 18s. 2d. Grants amounting to £180 had been made to Fellows from the Research Fund during the year.

Mr. TYRER proposed that the thanks of the Fellows be tendered to the Treasurer, for his services during the past year; this motion was seconded by Mr. D. HOWARD, and carried.

			<i>Expenses on Account of the Journal.</i>					
	£	s. d.		£	s. d.		£	s. d.
Balance at Bank March 16th, 1895.....	1,630	5 9	Salary of Editor.....	1,630	17 9	Salary of Editor.....	250	0 0
" in hands of Treasurer.....		0 12 0	Salary of Sub-Editor.....			Salary of Sub-Editor.....	200	0 0
<i>Receipts by Life Compositions, Admission Fees, and Subscriptions from March 16th, 1895, to March 21st, 1896.</i>			Editors' Postages.....			Editors' Postages.....	10	10 0
Life Compositions—2 at £30; 9 at £20; 1 at £15; 4 at £12; 8 at £10.....	428	0 0	Abstractors' Fees.....			Abstractors' Fees.....	7 8 11	
110 Admission Fees.....	440	0 0	Periodicals for Abstractors.....			Periodicals for Abstractors.....	281	5 4
Subscriptions for 1888 to 1891 at £2.....	6	0 0	Printing of Journal.....			Printing of Journal.....	14	16 6
" 1892 at £2.....	84	0 0	Distribution of Journal, by Printers.....			Distribution of Journal, by Printers.....	1,680	12 10
" 1893 at £2.....	300	0 0	Authors' Copies.....			Authors' Copies.....	327	19 6½
" at £1.....	2	0 0	" " " by Society.....			" " " by Society.....	9	19 5
" at £1.....	1,142	0 0	Colotype portraits of the late Professor Marignac.....			Colotype portraits of the late Professor Marignac.....	75	18 0
" 1895 at £2.....	2,020	0 0	Printing of Proceedings (including Indexes for 1893 and 1894).....			Printing of Proceedings (including Indexes for 1893 and 1894).....	184	9 6
" 1896 at £2.....	15	0 0	Distribution of Proceedings, List of Members, and Charter and Bye-Laws.....			Distribution of Proceedings, List of Members, and Charter and Bye-Laws.....	76	16 8½
" at £1.....	2	0 0	Publishers' Commission.....			Publishers' Commission.....		
" 1897 at £2.....	485	11 3	Advertising Agents' Commission.....			Advertising Agents' Commission.....		
Proceedings.....	6	7 6	<i>Expenses on Account of the General Index.</i>			<i>Expenses on Account of the General Index.</i>		
Proceeds of advertisements in Journal.....	19	9 6	Salaries.....	4,454	0 0	Salaries.....	261	6 2½
Subscription from the Society of Chemical Industry to June, 1895.....	7	7 0	Petty expenses.....			Petty expenses.....	49	18 10
" Society of Public Analysts to Jan. 1st, 1896.....	12	1 6	<i>Expenses on Account of the Library.</i>			<i>Expenses on Account of the Library.</i>	1	16 0
" Physical Society to Jan. 1st, 1896.....	20	9 6	Salary of Library Attendant.....	541	8 3	Salary of Library Attendant.....	154	2 4
Repayment of Income Tax.....			Books and Periodicals.....			Books and Periodicals.....		
Year's Dividends on £5,730 Metropolitan Board of Works ½ per cent. Stock.....	227	14 0	Binding.....			Binding.....	31	5 0
Year's Dividends on £4,000 Consols.....	106	6 8	Library Expenses.....			Library Expenses.....	182	16 3
Year's Dividends on £1,050 London and North Western Railway Debenture Stock.....	30	9 0	Salary of Assistant Secretary.....			Salary of Assistant Secretary.....	88	0 10
Year's Dividends on £431 1s. 9½ Cardiff Corporation Stock.....	12	9 11	Pension to Mr. Hall.....			Pension to Mr. Hall.....	4	15 3
Year's Dividends on £1,000 Bank Deposit.....	4	16 2	Miscellaneous Printing.....	39	18 0	Miscellaneous Printing.....		
			Printing List of Fellows.....	28	16 0	Printing List of Fellows.....		
			Charter and Bye-Laws.....			Charter and Bye-Laws.....		
			Stationery.....			Stationery.....		
			Expenses on account of Dinner on March 27th, 1895.....			Expenses on account of Dinner on March 27th, 1895.....		
			Repayment of Admission Fee and Subscription.....			Repayment of Admission Fee and Subscription.....		
			Congratulatory Address to the French Academy.....			Congratulatory Address to the French Academy.....		
			Mr. John Pinches: Striking Faraday Medal.....			Mr. John Pinches: Striking Faraday Medal.....		
			Honarium to the Faraday Lecturer.....			Honarium to the Faraday Lecturer.....		
			<i>House Expenses.</i>			<i>House Expenses.</i>		
			Providing Refreshments.....	381	15 9	Providing Refreshments.....	16	2 8
			Lighting the Building (gas, £15 19 0; electric light, £22 7 0).....			Lighting the Building (gas, £15 19 0; electric light, £22 7 0).....	41	6 0
			Heating " (coals).....			Heating " (coals).....	12	3 0
			Cleaning ".....			Cleaning ".....	30	0 0

1896.	<i>Assests.</i>	
Mar. 21st,		
Balance at Bank (current account).....	989	6 7
" " (on deposit)	1,000	0 0
" in hands of Treasurer	0	11 0
Metropolitan Board of Works 3½ per cent. Stock.....	6,730	0 0
2½ per cent. Consols.....	4,000	0 0
London and North Western Railway Converted Stock	1,050	0 0
Cardiff Corporation 3 per cent. Stock.....	1,520	14 3
		7,046 15 9

Bankers' Commission		1 7 3
Purchase of £431 1 9 Cardiff Corporation Stock		450 0 0
" " "		1,200 0 0
Treasurer's Stamps and Drafts	£1,089 12 6	6 11 4
Petty Cash Disbursements		0 1 0
" Assistant		10 0 0
" Office Postage Account		63 16 9
Secretarial Postages		4 16 0
Balance at Bank (current account)		989 6 7
" in hands of Treasurer		9 11 0
		7,046 15 9

Audited, with vouchers,
and found correct.
March 21st, 1896.

{ BERTRAM BLOUNT,
 H. BREBETON BAKER.
 } JOHN SHIELDS.

DR. THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.
FROM MARCH 16TH, 1895, TO MARCH 21ST, 1896.

1895.		1896.		1897.	
Mar. 16th.	Mar. 21st.	Jan. 8th, 1896.	Jan. 8th, 1896.	Jan. 8th, 1896.	Jan. 8th, 1896.
Balance at Bank, March 16th, 1895.....	£ 134 2 11	Grants to J. Walker.....	£20		
Year's Dividends on £4,400 Metropolitan Board of Works 3½ per cent. Stock.....	148 17 4	" " H. Ingle.....	10		
Year's Dividends on £1,000 North British Railway 4 per cent. Stock.....	38 13 4	" " J. J. Hummel and A. G. Perkin.....	30		
Donation from Lord Rayleigh (Honorarium to the Faraday Lecturer).....	20 0 0	" " B. Lean.....	10		
Repayment of Income Tax.....	14 15 5	" " J. J. Sudborough.....	10		
		" " R. E. Doran.....	5		
		" " E. Haworth.....	15		
		" " H. Bone.....	15		
		" " C. F. Cross and C. Smith.....	10		
		" " F. D. Clattaway.....	15		
		" " Jocelyn F. Thorpe.....	20		
		" " J. E. Marsh.....	10		
		" " A. E. Tutton.....	10		
		Balance at Bank.....	65 0 0		
			176 9 0		
			£356 9 0		

The TREASURER, in responding, proposed a vote of thanks to the auditors.

Mr. A. BLOXAM seconded the motion, which was unanimously adopted, and acknowledged by Mr. B. BLOUNT.

Dr. RUSSELL, F.R.S., proposed a vote of thanks to the Officers and Council.

Professor TILDEN, F.R.S., seconded the motion, which was unanimously adopted.

Professor THOMSON responded.

Professor McLEOD, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, and Abstractors, which was seconded by Dr. THORNE, and carried.

Mr. GROVES, F.R.S., responded.

Dr. J. Voelcker and Mr. Nagel were appointed scrutators, and a ballot was then taken for the election of Officers and Council for the ensuing year. The following were subsequently declared duly elected:—

President : A. Vernon Harcourt, M.A., LL.D., D.C.L., F.R.S.

Vice-Presidents who have filled the office of President : Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, LL.D., Ph.D., F.R.S.; A. Crum Brown, D.Sc., M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, K.C.B., Ph.D., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

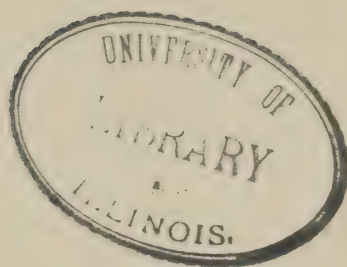
Vice-Presidents : Horace T. Brown, F.R.S.; James Dewar, M.A., LL.D., F.R.S.; Francis Robert Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; W. Chandler Roberts-Austen, C.B., F.R.S.; William A. Tilden, D.Sc., F.R.S.

Secretaries : John M. Thomson; Wyndham R. Dunstan, M.A., F.R.S.

Foreign Secretary : Raphael Meldola, F.R.S.

Treasurer : T. E. Thorpe, LL.D., F.R.S.

Other Members of Council : P. Philips Bedson, D.Sc.; Bennett Hooper Brough; Bernard Dyer, D.Sc.; Otto Hehner; Herbert McLeod, F.R.S.; H. Forster Morley, M.A.; G. Harris Morris, Ph.D.; James Wyllie Rodger; W. A. Shenstone; Arthur Smithells, B.Sc.; Thomas Stevenson, M.D.; Sydney Young, D.Sc., F.R.S.





A. W. Hofmann

HOFMANN MEMORIAL LECTURE.*

(DELIVERED MAY 5th, 1893.)

XLII.—*Personal Reminiscences of Hofmann and of the conditions which led to the establishment of the Royal College of Chemistry and his appointment as its Professor.*

By Lord PLAYFAIR, G.C.B., F.R.S., &c.

I BELIEVE it is desired that I should show what were the conditions that led up to a separate College of Chemistry in this country under the illustrious Hofmann, and that I should preface my remarks by some memories of the great chemist's early days at the famous University in Giessen, where I studied with him. My few words will only be introductory to the more valuable observations of those chemists who worked and co-operated with him in this country.

Hofmann was about two years my senior in age; nevertheless he did not begin his chemical training in Liebig's laboratory till after I had left it. Chemistry was not the profession which it was originally desired that he should follow. He first intended to pursue a career in philology and law, and studied these subjects at the University, and his training in languages stood him in good stead in after life; indeed, I have heard him make excellent speeches in several languages—I recollect one instance especially, in 1867, when the French chemists gave a memorable banquet to the chemists of foreign countries: I was entrusted with the thanks of the invited guests, and spoke in English, while Hofmann, in proposing the health of the French chemists, made a capital French speech.

When I first knew Hofmann at Giessen he was studying mathematics and physics, and, though he mixed in a friendly way with the active investigators in Liebig's laboratory, he was not one of our body. When he did enter that great laboratory, he had a groundwork of general culture and physical science that helped him greatly in his subsequent career. With that I have nothing to say except in relation to his influence on English chemistry.

But I must diverge from the immediate subject of my memoir to recall to mind the position of English chemistry, in order to explain why the advent of Hofmann to this country became such an important

* Chemical Society's Memorial Lectures, No. III. Compare *Proceedings of the Chemical Society*, 1893, p. 132.

event. England has never been deficient in great chemical investigators, but has lacked practical schools for training them. Indeed we can claim with perfect justice that a large number of the discoveries which have made chemistry a science have originated in this country. The last century was especially prolific. The capital discovery of oxygen and the other pneumatic discoveries of Priestley; the studies of airs and of latent heat by Black; the discovery of the composition of water simultaneously by Cavendish and Wedgwood; the work of Dalton, extending into the last and present century, by which he brought law and order into our ideas of chemical combination: all these were radical discoveries forming the very foundations of chemistry.

In the present century I have again to begin with Dalton, for it was my good fortune to know him intimately, and I can never forget his venerable figure, supported on the arm of Dr. Joule, coming daily to hear my lectures at Manchester on the new organic chemistry, which had arisen in then recent times. Dalton, Davy, Faraday, and Graham indeed stand out as shining lights in our century. Davy and Faraday were brilliant investigators, and both of them had a singular charm and eloquence as lecturers. To them we owe largely the popularity of chemistry in this country. But none of these chemists, except Graham, thought of opening their laboratories for the training of students in the methods of research. That was reserved to my own master, the celebrated Thomas Graham. I was a student in his laboratory in Glasgow in 1835 and 1836, and followed him to London as his private laboratory assistant in University College. Graham's example spread, and several Colleges, and even the Universities, slowly adopted the view that laboratories were necessary to teach and to train the chemists of the future.

At that time organic chemistry was little known or studied in this country, and all of us who had means to go abroad used to flock either to the laboratory of Liebig at Giessen or to that of Wöhler at Göttingen. I need not point out that Baron Liebig exerted an enormous influence on the progress of organic chemistry, both by his own discoveries and by those of his pupils from all countries, who were trained to do researches in his celebrated laboratory. Many English students studied in it, and when they returned to England they were imbued with the enthusiasm of their master, and acted as missionaries in spreading a knowledge of the new organic chemistry. Soon laboratories for teaching students were opened in various parts of the country.

In 1840 Liebig published his celebrated work, *Chemistry of Agriculture and Physiology*. It is difficult to-day to realise the effect that work had in promoting the study of chemistry: it greatly

increased, the demand for laboratory teaching and even the older universities found it necessary to provide means for laboratory training.

Two years after its publication, in 1842, the illustrious Baron Liebig made a sort of triumphal tour in this country. He visited the Prime Minister, Sir Robert Peel, at Drayton Manor, and paid other visits to the great agriculturists of the day—Lord Spencer, Lord Ducie, Lord Fitzwilliam, Mr. Pusey, and many others, as well as to most of the chief towns. At all places meetings were held, and Liebig, with his travelling companion, the genial and celebrated geologist, Dr. Buckland, had opportunities of disseminating his views on the importance of chemistry to mankind. The tour was a personally conducted one, like Cook's tours in the present day: the conductor and interpreter of the party, in fact, was a young man called Lyon Playfair, who took care that the effects of the tour should be felt in all the chief centres of Great Britain.

The immediate effect of Liebig's tour was to make chemistry a popular science, and to induce colleges to open laboratories for teaching it. The School of Mines was opened in Jermyn Street with, for the time, an excellent laboratory, which was always filled with students; still, its purposes were chiefly limited to the professional objects of the college. University College and King's College gave much attention to laboratory teaching. The popular wave of 1842-43 did not soon expend its force, and in 1845 the Royal College of Chemistry arose.

I have mentioned these facts to show that the time had come to open a special college of chemistry. It could not have been created sooner than it was, because the demand would have been too limited. Two wise men deserve the chief credit for its foundation: I need scarcely say that they were the Prince Consort and the Queen's physician, Sir James Clark. As I had the honour and privilege of a long continued friendship with both of these great men, I may with advantage explain their reasons for desiring to found a special college of chemistry. They saw that all the chemical laboratories in existence in this country were mere accessories or subordinates to professional training; the students who entered them rarely desired to become chemists, but only wished to learn as much of the science as would be useful to them in their professions of doctors, lawyers, or engineers. This limitation sometimes took an exaggerated form, as it did in the case of a Turk, for example, who joined my laboratory and then told me he wished to learn no more chemistry than would help him to explain the doctrines of Paracelsus. The promoters of the Royal College of Chemistry therefore desired to found an institute apart from professional requirements, in which chemistry would be

studied for its own sake, with the expectation that many students might follow it as the occupation of their lives, and have an ambition to widen its boundaries by research. A college of this kind, without endowments, could not have been created unless there had been a strong popular feeling in its favour, and I have tried to show how that arose through Liebig's influence.

Science belongs to no country, and the reputation of Hofmann and the recommendation of Liebig clearly pointed him out as the director of the new college. He had qualifications of a remarkable kind for the position. As a teacher he was singularly interesting and lucid. He marshalled his arguments with great care, and as he brought them towards the conclusion, he increased in his persuasiveness and seemed to each individual student to take him into his special confidence as to the result. The lucidity of his explanations was admirable. I would quote as an instance his lecture on the metrical system of weights and measures; this lecture was the very best exposition of the subject that I have heard. A lucid power of exposition was essential to the teacher of a special school of science, but it was not the chief element of Hofmann's success. Enthusiastic as an investigator of scientific problems, he could impart his enthusiasm, if not his genius, to others: his pupils were led to extend his researches with great success, and to enlarge the boundaries of science in the directions which he indicated. If the College of Chemistry were as successful as I claim it to be, you may ask why did it disappear? It had no endowments, and depended to some extent on popular subscriptions. These were easy to obtain when chemistry had the temporary popularity which I described. Every landowner then thought that agricultural chemistry was to be his salvation. Liebig's book was not a muck manual, and did not produce the expected results; the College of Chemistry, however, went on its even course of promoting science for its own sake, but the support gradually dwindled.

At this time, fortunately, I resigned my professorship, and Hofmann succeeded me, carrying with him his college as the laboratory of the School of Mines. This was inevitable under the circumstances, but it was not good for the College of Chemistry or for science. The original success of the college was due to its separate and independent existence: its absorption into the School of Mines contracted its original ideas, and made it subordinate to professional needs. No doubt Hofmann felt this, for he left England in 1864 to take up a professorship in Berlin.

I hope that I am not too sanguine, but I should like to live to see a new college or institute of chemistry arise, like a Phoenix, from the ashes of the old one. Will the new Commission for a London

University stir among the not yet cold ashes of the old College, and allow the Phoenix to escape? If it is to be permanent, it must rest on endowment, and science will find another great man to act as Director. Such aspirations may not improbably be carried into effect, though their realisation may be delayed. When Lawes, with true munificence, determined to benefit agriculture by laboratory research, a Gilbert was at hand capable of carrying out his ideas. We may hope that the Chemical College of Hofmann may appear again in a new and more permanent form in connection with higher university teaching in London, as a supplement to, and not in competition with, the excellent laboratories in our colleges.

I now yield my place to the pupils of Hofmann. They will tell you how precious his labours have been to the advancement of the science which we love. This is of infinitely more importance to the world than the incidental advantages which flow from the practical applications of abstract science. Nevertheless Dr. Perkin will, no doubt, tell you some interesting and startling facts in relation to these. Hofmann's first research in the Giessen laboratory was upon the nature of coal tar. When he became Director of the College of Chemistry, he continued his researches, thinking of science only, not of practice. From them arose the great tar industry, especially in its relations to the production of colours. Though these originated in this country as an important industry, the Germans, from their better technical education, have now secured nearly nine-tenths of the production of artificial colours.

Hofmann's discoveries are our heritage in science. It is useful to us all to hold such an In Memoriam celebration as this. In reviewing Hofmann's successful life, which has so enriched the fields in which he laboured, both old and young feel that we should like to live as he lived. In thinking of Hofmann, I recall one of my favourite verses, by Bailey.

“ We live in deeds not years ; in thoughts not breaths,
In feelings, not in figures on a dial.
We should count time by heart throbs. He most lives
Who thinks most, feels the noblest, acts the best.”

The History of the Royal College of Chemistry and Reminiscences of Hofmann's Professorship.

By Sir F. A. ABEL, Bart., K.C.B., F.R.S., &c.

NOT from any unwillingness to undertake what can only be regarded as a labour of love, but from a conviction of the inadequacy of my powers, under overwhelming pressure of official work, to worthily accomplish that labour, have I hesitated to accept the task which my colleagues of the Chemical Society, and old fellow students of the Royal College of Chemistry, have pressed upon me, of placing on record some incidents connected with the earlier part of the career in London, of my beloved and revered master and friend, the late August Wilhelm von Hofmann. And, when I recall to mind the interesting account of the difficulties overcome in securing to England the services of the courageous and enthusiastic worker—that masterly organiser and matchless teacher—which his distinguished pupil, Dr. Tiemann, included in the admirable memorial-address delivered to the German Chemical Society last autumn, and the graphic outline which Hofmann, the real founder of the College of Chemistry, himself published, in 1871, of the early history of that school, under the title of *A Page of Scientific History*, I feel that it will indeed be difficult to impart to my brief recital any semblance of novelty, or any interest, additional to that which, for his many pupils, admirers and friends, invests all the circumstances of Hofmann's career, or which may, perhaps, attach to such circumstances as that the narrator of this fragmentary sketch was one of the first students whose names were inscribed upon the register of the College of Chemistry, even before the services of Hofmann had been secured to it; that he was the first fortunate individual who was selected by the master from his pupils as assistant, and that, during the first five years of the struggling but vigorous existence of the New National School of Chemistry, it was his privilege and pride humbly to imitate, to the utmost of his youthful powers, the indefatigable devotion of the enthusiastic teacher to the interests of the School and its students, and, at the same time, to carry on the experimental work connected with some of the brilliant researches which, during that period shared, with his pupils, the untiring energies of that prince of investigators and giant for work.

To Lord Playfair, the fellow student, colleague, and firm friend of Hofmann, we are greatly indebted for the interesting sketch with which he has favoured us, of the position of chemical instruction in

Great Britain at the period when the idea was first conceived, fifty years ago, of establishing an English School of Practical Chemistry, upon the basis of Liebig's School at Giessen, which, at that time, had acquired a world-wide reputation, and to which students resorted from all parts of the world.

The commencement of my own career as a chemist affords no bad illustration of the difficulties attending attempts by young beginners with very limited resources, to acquire a knowledge of practical and analytical chemistry, with a view to adopting the science as a profession, half a century ago. The two or three establishments where chemical tuition was pursued to a very limited extent, were closed to young aspirants of that class; and, when my father remained undeterred by the advice which my subsequent good friend, the late Robert Warington, gave him, not to think of letting his son pursue the study of chemical science as a future means of livelihood, on account of the very limited prospects of advancement in the profession, the Royal Polytechnic Institution presented itself to him as the only place at which the fees demanded were within his means. I accordingly entered the laboratory of that dispensary of so-called popularised science, dazzled by the prospects of a brilliant future, presented to me by the clever popular lecturer of that time: only, to find that not even an attempt was made to impart to the deluded youngster the fragmentary superficial information of the Professor, and that the sole means which were left to him of acquiring some practical chemical knowledge, consisted in plodding, unaided, through Brande's *Manual*, endeavouring to acquire experimental skill by preparing the elements and their compounds, according to the directions there laid down, and to become acquainted with analysis by following the instructions for applying tests given in tabular form by Andrew Parnell. At the expiration of six months' struggle to work steadily in this fashion, amid surroundings by no means conducive to perseverance, I quitted the Institution (in February, 1845), armed with a testimonial certifying that my "analyses and experiments had always been conducted with great skill and minuteness," and that the Professor could "confidently recommend Mr. Abel to any appointment where a knowledge of practical chemistry may be required." Failing to realise that my practical chemical education had attained the degree of completeness portrayed by this description, I hailed with joy the tidings that a School of Chemistry was about to be established in London upon the Giessen type. Several other young men, who afterwards became prominent pupils of Hofmann, were in a similar position at that time, and so, when the temporary laboratories of the new college were opened in the autumn of 1845, there was a small band of aspirants impatiently waiting to

avail themselves of the benefits of the system of instruction which had already acquired so high a reputation on the Continent.

The importance of establishing in England an institution where the systematic study of chemistry, as a profession in itself, could be pursued, and where not only the acquirement of proficiency in systematic chemical analysis, but also the attainment of a knowledge of the art of chemical research, could be placed within the reach of a student of moderate means, had then become recognised by some prominent public-spirited men in England, mainly, in the first instance, through the intelligent representations and indefatigable exertions of Dr. John Gardner, the translator of the admirable little work of Liebig's, entitled *Familiar Letters on Chemistry*, which most usefully contributed to awaken the public mind to the benefits to be derived from the pursuit of chemical research. Dr. Gardner was zealously assisted in his first endeavours to place the scheme upon a practical footing, by his intimate friend, Mr. J. Lloyd Bullock, one of Liebig's earlier pupils, a fellow student of Hofmann's at Giessen, who, already in 1843, was the head of a prominent pharmaceutical business in Conduit Street, and is now, at the ripe age of 82, almost as hale and active in mind and body as he was in those days. He recently directed my attention to the following incident in the early history of the College of Chemistry, of which I believe very few of those who have since been connected with that school have any knowledge.

The sympathies of a number of prominent men had been enlisted, and promises of substantial support obtained, in 1843, in favour of a proposal to establish in London a National Practical School of Chemistry, by means of a very skilfully prepared prospectus; it was there pointed out that the progress of Liebig's Giessen School had been watched with deep interest in England, where the researches of that great chemist and his pupils had already given a most important impetus to agriculture and national industries; so that the want of such a school in this country, and the benefits which would accrue therefrom in manifold directions, could not but be recognised. In the autumn of that year Messrs. Gardner and Bullock induced the then Professor of Chemistry at the Royal Institution, Mr. W. T. Brande, to bring this prospectus before the managers, together with a carefully prepared scheme for establishing the scientific section of a British School of Practical Chemistry within the walls of the Royal Institution. In the preparation of this scheme, Messrs. Gardner and Bullock must evidently have had the assistance of Professor Brande, who appears to have been favourably impressed with the proposal.

The appointment of a Standing Committee of Management was

proposed, to consist of members of the Royal Institution and other men of science, of agriculturists, medical men, and of chemists and druggists. One of the earliest steps to be taken was to approach the Government through the Board of Trade, with the view of obtaining State aid. The fees to be charged to students were to be fixed at a very moderate amount, it being proposed to support the School by funds independent of those derived from fees. When these funds had been secured (to quote the scheme) the School was to be "established upon a broad basis"; the scientific section was to be capable of receiving 30 or 40 pupils; a Professor was to be appointed at a salary adequate to secure his undivided attention to the great purposes of the School; and it was considered that, if a thoroughly competent man were appointed from one of the great German Schools, a commencing salary of £250, with a liberal share of the students' fees, would offer sufficient inducement to secure the services of a man of acknowledged eminence.

The scheme proceeded to indicate that the premises in Albemarle Street were adequate to provide a capacious laboratory, where chemical science could be practically taught, and in which each student would have a separate working bench; the establishment was to include a private room and laboratory for the Professor, a balance room, an apparatus room, and store rooms. The plans for fitting up the laboratories were given in some detail. The scheme included the provision, apart from the scientific school, of a practical laboratory for the pursuit of studies on the most important applications of chemistry; this it was proposed should be placed under the direction of Mr. Lloyd Bullock, subject to the supervision of the Professor, and it was to be established in capacious apartments in George Street, Hanover Square (which became the temporary laboratory of the College in 1845). Mr. Bullock proposed to offer his services for the benefit of the practical school gratuitously. Lastly, it was considered that the provision, by subscriptions or grants, of an annual income of £800 to £1,000, would suffice for the maintenance of the School.

The managers of the Royal Institution referred this scheme, in November, 1843, to Professors Brande and Faraday, who reported favourably on the objects of the proposed School to the managers at their meeting on the 4th December, 1843. Messrs. Gardner and Bullock were therefore invited to attend to give explanations, and it was afterwards resolved that the subject be again referred to the Professors for a further report, which was presented by them on December 19th. In this report, after a brief discussion of the scheme, Messrs. Brande and Faraday stated that the existing laboratory in Albemarle Street, with the room and cellars beyond, would appear

to afford sufficient accommodation for the scientific school. The School of Chemistry (lectures) for medical students and others, conducted by Mr. Brande, would be thereby displaced, but, from consultation with Mr. Vulliamy, he was satisfied that accommodation for his courses could be provided in the Model Room, the models being transferred to the Battery Room. It appeared, therefore, "that place *could* be made for the School in the Royal Institution, but at a loss of many conveniences to itself and its Professors."

The words with which the report concludes illustrate in how thoroughly impartial a manner the eminent Professors of the Royal Institution dealt with a proposal which, if carried into effect, could not but have seriously interfered with their convenience and comfort in the pursuit of their work at Albemarle Street, and especially so in the case of that indefatigable investigator the resident Fullerian Professor of Chemistry. They say—

"The result of our consideration is strong approval of the end proposed, and a desire that it may be carried out in the Royal Institution if it can be done well. We venture to submit our impression in such a form to the managers that, if approved, the degree of approbation and assistance which the Royal Institution may be willing to give be expressed as follows:—

"Considering the great object of the advancement of chemical science and of good to the community contemplated by the establishment of the proposed School, and the perfectly disinterested intentions and views of its promoters and supporters, the Royal Institution is willing and anxious to aid such an object as far as it can, consistently with the rights and privileges of its members; and if hereafter the proposers are in possession of names of supporters and pecuniary means sufficient to carry out the objects proposed, the managers will on their part be prepared to recommend to the members of the Royal Institution the appropriation of apartments in the house for the purposes of a scientific laboratory for the proposed School."

The report of the Professors evidently received very careful and anxious consideration by the managers, and the subject was also exhaustively discussed in correspondence between the Secretary, the Rev. Mr. Barlow, and the President, Lord Prudhoe (afterwards Duke of Northumberland). Upon a resumption of the discussion on the report, the week following its presentation, Professors Brande and Faraday informed the managers that after a closer examination of the limited space within the walls of the Royal Institution, and a careful consideration of the room required for the great and increasing stock of apparatus, minerals, and books, it appeared to them impracticable to afford accommodation to the proposed School,

whereupon the managers requested the Secretary to intimate to Messrs. Gardner and Bullock their regret that the space at their disposal was too limited to justify them in acceding to their request.*

The indefatigable promoters of the scheme for the establishment of the British School of Practical Chemistry did not relax their exertions after the failure of their negotiations with the Royal Institution, and continued to secure important accessions to the list of its supporters. At a public meeting held at the temporary offices of the College of Chemistry in St. Martin's Place, on the 29th July, 1845, a definite form was given to the proposed Institution, and, after the election of a Council and certain executive officers, the first, all-important, subject which received anxious consideration was the appointment of a Professor. One of the earliest and most prominent supporters of the movement was the amiable and accomplished Physician in Ordinary to the Queen, Sir James Clark, Bart., who became at the outset one of the staunchest and most active workers in the interests of the College of Chemistry, and an invaluable friend of the first Professor, and who was soon afterwards associated in both capacities with the Hon. William Bingham Baring, afterwards Lord Ashburton.

In Hofmann's interesting *Page of Scientific History* he points out that there was at that time no lack of most excellent chemical lecturers in England, and that, indeed, the style of experimental lecture-illustrations in general use in England was greatly superior to that which then prevailed in Germany and other parts of the Continent; but that the greatest want felt was easily accessible, efficient instruction, not only in systematic chemical analysis, but also in methods of conducting experimental inquiry, and it was with a view to meet this want that it was decided to follow the counsel of Sir James Clark, and apply to Liebig to select a suitable man from among his own assistants or past pupils for the appointment of Professor to the new College.

The story of the circumstances which secured the services of Hofmann for the foundation and development of the College are graphically narrated by himself in his *Page of Scientific History*. The refusal of the appointment successively by Fresenius, then already Professor at Wiesbaden, and by Will, Assistant Professor at Giessen, and the desire of Hofmann, at that time "Privat Docent" at Bonn, to accept it, mingled with the natural hesitation

* Since this was read to the Chemical Society, in May, 1893, the proposal favoured by Professors Brande and Faraday has been thoroughly realised, through the munificence of Mr. Ludwig Mond, by the establishment of the "Davy-Faraday Research Laboratory," adjoining the Royal Institution, and under the direction of its managers.—F. A. A.

to risk, through the occupation of a possibly precarious position, the serious interruption of a bright career just commenced at the Rhenish University; the happy solution of the difficulty through the gracious and invaluable intervention, at the instigation of Sir James Clark, of the late Prince Consort, who had from the first taken a warm interest in the proposed establishment of the English Chemical College, and who happened to be staying with the Queen at Brühl when the negotiations were proceeding; the appointment of Hofmann as Extraordinary Professor at Bonn, accompanied by an immediate grant of two years' leave of absence, so that he might at once re-enter upon his career in Germany should the English enterprise fail; his speedy departure for England, and the commencement of operations in the temporary laboratories of the College of Chemistry in George Street, Hanover Square, in October, 1845: all these incidents in the early history of the College have been recounted in interesting detail by Hofmann himself and by his pupil and brother-in-law, Dr. Tiemann.

For the first session, 26 students had entered, and among these were Warren de la Rue, F. A. Abel, E. C. Nicholson, Henry How, Thomas Rowney, C. L. Bloxam, and Robert Galloway. The laboratories in George Street were fitted up in temporary and very economical fashion, and I well remember the energetic way in which Hofmann set to work immediately upon his arrival in London, aided by the amiable young Herman Bleibtren, whom he had brought with him as a temporary assistant, and whose quaint semi-military attire and imperfect English were a little trying to the powers of control of some among the younger students of the first session.

Hofmann's complete sway over his pupils was at once secured by his indomitable perseverance and inexhaustible patience with the dullest, his earnestness of manner—his clearness of exposition, rendered additionally attractive by an inherent quaintness and a power of happily rendering German expressions into graphic English. Those first two sessions of the College, in the scantily equipped laboratories, with makeshift contrivances of the crudest character, and an utter absence of any convenience for conducting investigations, must have been a sore trial of patience and powers of endurance to the impetuous young teacher, and to the enthusiastic worker, whose only recreation was the pursuit of original research. When to these circumstances is added the mental strain involved in the almost continuous pursuit of instruction and discussion in a foreign language for at least eight hours daily, to say nothing of continued anxious consultations with the Council and officials of the College regarding ways and means; the heavy work connected with the erection and equipment of the permanent laboratories; the grappling

with the problems of maintaining and fostering public interest in the Institution, and of keeping current expenses within very moderate bounds,—it is self-evident that no small moral courage and powers of endurance were needed for the successful accomplishment of these duties, and for the maintenance of the confident and apparently light-hearted demeanour, and of the power of instilling into others confidence of future success, which were peculiarly characteristic of Hofmann in those days of supreme difficulty. But these very characteristics, added to his genial and charming manner, high flow of spirits, and originality in conversation and correspondence, secured to him devoted friends, not merely among colleagues and pupils, but in whichever direction social intercourse was opened up to him. Just as his earnestness of purpose and enthusiasm kindled corresponding qualities in a large proportion of his pupils, so also his sanguine temperament and airy treatment of difficulties maintained, among many of the early friends and important patrons of the struggling Institution, a steadfastness of purpose which otherwise would doubtless have speedily waned.

Among the most prominent of the first students at the College, there was one who at once exercised a very marked beneficial influence in establishing a spirit of emulation, combined with good fellowship, among the younger students, and who speedily became one of Hofmann's most intimate and most useful friends; it is almost needless to say that I refer to Warren de la Rue. A bright example to all in industry and unflinching perseverance, manipulative skill, and methodical work; of calm courage and presence of mind in the face of sudden emergencies such as are bound to arise occasionally in laboratories where a great variety of experimental work is in progress; the embodiment of amiability, ever ready to lend a helping hand, in whatever direction it might be needed; now acting as sagacious adviser in difficulties; now as arbitrator in disputes or differences which would occasionally arise between fellow students; always active in the interests of the school;—no man could have made himself more universally beloved than De la Rue. There can be no doubt that he laboured as importantly, as he did unobtrusively, for the good of the College in the days of its greatest troubles, and was a powerful support to the Professor in *his* constant battles against formidable difficulties with which, suddenly launched as he had been upon a new career in a strange land, he would indeed have found it much harder to grapple successfully, in the absence of two such trusty friends and able supporters as Sir James Clark and Warren de la Rue.

There is but one opinion among those who can appreciate the stupendous difficulty of the task so brilliantly accomplished by Hofmann, in placing the College of Chemistry upon a sure foundation,

and in securing to it, within a very few years, a high position among the chemical schools of Europe ;—that his success was ascribable to the possession of a happy and rare combination of the highest talents as a teacher with exceptional powers as an investigator, inexhaustible industry and energy, and an enthusiasm not to be subdued by any obstacles ; a characteristic quality possessed in the highest degree by his great master, Liëbig.

It was Hofmann's rule, to which, during the continuance of my stay at the College he strictly adhered, to visit each individual student twice during the day's work, and to devote himself as patiently to the drudgery of instructing the beginner, or of helping on the dull scholar, as he did, delightedly, to the guidance of the advanced student, whom he would skilfully delude into the belief that the logical succession of steps. in making the first investigation which the master had selected for pursuit by the pupil, was the result of skill in research which he had already attained, instead of being simply or mainly the skilful promptings of the great master of original research.

It was not until the work of the College had been well established in the new laboratories in Oxford Street that Hofmann began to give courses of lectures ; but even in the first session he would occasionally deliver, at the bench of a particular pupil, short expositions of certain subjects, addressed to the body of the students in the laboratory, which were very attractive in style and matter, and always listened to with great attention.

In some interesting notes about Hofmann, which have been very kindly shown to me by Professor McLeod, who was his favourite lecture-assistant some considerable time after I had quitted the College, he testifies to the remarkable knowledge of English, and powers of expression therein, possessed by Hofmann ; to the attractiveness of his manner, and to the way in which he carried his audience with him by his enthusiasm ; so that his great tendency to exceed, and somewhat considerably, the usual hour, never gave rise to impatience or fatigue with the young students. He devoted much time to the suggestion or contrivance of lecture illustrations, and was very particular in having his discourses appropriately, but not profusely, illustrated by experiments.

To return to the early days of the College : its promoters having succeeded in securing premises in Hanover Square suitable for official and residential purposes, with an open space in the rear, facing Oxford Street, plans for a set of commodious laboratories were speedily prepared under Hofmann's guidance and with valuable aid from Warren de la Rue, and the first stone of the building having been laid by the Prince Consort on the 16th June, 1846, the third session of the College was actually commenced in the new labora-

tories in October of that year. In the second session, beginning in March, 1846, 37 fresh students had entered, making 63 in all, and the two small temporary laboratories in George Street became inconveniently crowded. Among the new men were the much-beloved and lamented Charles Mansfield, whose terrible death affected Hofmann deeply; Frederick Field, Poet Laureate of the College, who became one of Hofmann's favourite pupils; George Merck, of Darmstadt; Henry M. Noad, and Bransby Cooper—all, long since, passed away. At the beginning of this session I was appointed by the Professor to help Dr. Bleibtreu, and afterwards Dr. Blyth, in the work of elementary instruction, and of maintaining the equipment of the temporary laboratories, and, towards the close of that session, two of my fellow students (dear friends of mine, whom their master long outlived) were selected by the Professor for similar posts of honour and hard work; Edward Chambers Nicholson, and the comparatively very youthful pupil Charles Loudon Bloxam; the first possessed of veritable genius as a *preparateur* (having already acquired some considerable skill during a brief apprenticeship in the business of Mr. Lloyd Bullock); the second, exhibiting at the very outset a marked predilection and talent for tutorial work.

A highly busy time we three young fellows had of it during the summer vacation of 1846, in the back kitchen and scullery of the house in Hanover Square (the George Street laboratories being in course of dismantlement), preparing the material for stocking the sets of reagent-bottles for over 60 students; finding time also for a little special experimental work. Thus, Schönbein having then recently published his instructions for the production of gun-cotton, I prepared a somewhat considerable quantity of that material (little dreaming that, 15 years later, I should begin to become in some measure identified with it); and the small remnant which I have still preserved of that preparation, bears witness to the care with which its purification was accomplished and consequent stability secured by the young student. Our activity in the basement of the College premises in Hanover Square during the summer and autumn of 1846 must, however, have been less to the taste of the immediate neighbours than to ourselves and our Professor, for, in the minute-book of the College Council, is recorded a resolution, dated October of that year, directing the immediate removal of all chemicals and laboratory operations from the kitchen and other apartments into the laboratory.

The new establishment in Oxford Street included a small private laboratory for the Professor, and, before the close of the year. Nicholson was already busily engaged therein upon the work of research which Hofmann at once resumed with an ardour intensified

by the compulsory abstention from the delight of his life—to which he had been compelled for a time to submit. The first investigation upon which Nicholson had to work was on the action of cyanogen on aniline, toluidine, and cumidine, while he, at the same time, carried out, under Hofmann's direction, his own first investigation on the compounds of phosphoric acid and aniline. My time was divided between the duties of teaching, which I shared with Bloxam as my junior (for a time under that most amiable and painstaking teacher, Dr. John Blyth, who had been appointed Assistant-Professor), and the work of another branch of Hofmann's prolific aniline researches, viz., the investigation of the action of chloride of cyanogen and bromide and iodide of cyanogen upon aniline (from the effects of which my eyes suffered permanently). At the same time, I also carried out my first organic investigation and the analysis of the mineral waters of Cheltenham. In the latter and other analytical research work I became associated with another fellow-student, Thomas H. Rowney, whom Hofmann appointed as his first lecture-assistant.

It is difficult to estimate the full value, to the individual concerned, of the severe work, and the many-sided training, which an assistant of Hofmann experienced, more especially in those earliest days in the history of the College of Chemistry. Dr. Tiemann quotes from important materials for a biography of Hofmann which Dr. Max Kopp has prepared, the following words of the latter in referring to some of his former master's earlier stupendous investigations:—“Thank God, what cause we have to admire, besides our master, the patience and powers of endurance of the assistants of those days;” and certainly the work which we then accomplished in the arduous but happy life we led was well worthy to be called hard work. As an illustration, I venture to sketch, in a few words, the routine which for five years I pursued as assistant at the College of Chemistry. A walk of about five miles brought me to the College before nine, the students' hours being from nine to five. The work of teaching, and attention to the requirements of the students, then went on continuously, simultaneously with the conduct of research work, and with the incidental production of materials for that work. One-half of my table in the principal laboratory was devoted to the operations connected with the Professor's investigations; the other half to my own researches. Ever and anon a student would come for assistance and advice, which led to my experimental work being of a somewhat perplexingly intermittent character. Hofmann began his first round among the students at half-past nine, and, having completed this, he divided his attention between the research work in Nicholson's hands and that with which

I was entrusted. A roll and butter or some biscuits, devoured while work was going on, constituted my midday meal, and I reached home at half-past six, frequently returning to the laboratory in the evening to carry out combustions (which Nicholson and I learned to do in couples, with charcoal fires, be it remembered) or other special operations, or to work out results, discuss them and prepare papers, with the Professor, or to make some progress with my own investigations, returning home late at night. When not thus employed, the evenings were devoted to the coaching of students, at from three to five shillings the hour, or to literary work, such as the translation of the *Jahresberichte* of Liebig and Kopp, for its English editors, Hofmann and De la Rue, so as to supplement the magnificent income of £40 a year, upon which we assistants were "passing rich." One evening weekly we had a students' meeting for papers and discussions, which Hofmann used to make a point of attending and taking part in. When the two months' vacation-time came round, we assistants used to take, at the most, a fortnight, for there was much to be done to prepare the laboratories for the next session's work; and, before his departure for his well-earned holiday in Germany, the Professor left his assistants a liberal allowance of work to be performed by his return: such as the preparation of a supply of aniline from indigo, the development of new methods for the production of materials for his researches, the analyses of new products, or the construction of special apparatus. But the life, although somewhat arduous, was a thoroughly happy one; who would not work, and even slave, for Hofmann? It was a rich reward to receive a word of commendation of a skilfully constructed piece of apparatus (for in those days very much had to be accomplished with tubes and corks and sheets of india-rubber); or to hear an expression of contentment at a successful distillation for aniline (the production of a few ounces being a proud achievement); or the attainment of a good instalment of analytical results. Hofmann highly appreciated skilful work; manipulative dexterity being his weak point (he used to tell us that, in his student's days, all his fingers were thumbs, and that he could hardly handle a test tube without "scrunching" it). There was an indescribable charm in working with Hofmann; in watching his delight at a new result, or a successful operation; or his pathetic momentary depression when failure attended the attempt to attain a result which theory indicated. "Another dream is gone," he would mutter plaintively, with a deep sigh; but not for long was he despondent. "Never mind," he would soon exclaim, "we shall have it to-morrow!" His inherent buoyancy of spirits helped him through all trials, of which those relating to official and personal concerns, or domestic sorrows, of

which he experienced many in quick succession, were apparently as nothing compared with the failure, for the time, to achieve the result which his sagacity predicted, and which sooner or later he attained.

The students who, during my career at the College, which terminated early in 1851, were advanced by Hofmann to the post of Assistant, partly to help with the general work of instruction and to prepare and assist at his lectures, and partly to work at his researches, were Abel, Nicholson, Bloxam, Rowney, Brazier, and Medlock; several of my colleagues left soon after my departure, and the subsequent roll of student-assistants included many names since well known in the scientific world, and many old Fellows of the Chemical Society: Crookes, Spiller, Tookey, Reginald Morley, J. S. Abel, Ansell, Church, Matthew Johnson, H. M. Witt, McLeod, Groves, Valentin, Barrett, Bassett, Vacher, O'Sullivan, and Reynolds; and the private assistants, who were exclusively employed upon his researches, embraced a succession of well-known German names, of which several have become famous: P. W. Hofmann, Fischer, Fries, Bopp, Griess, Förster, Ulrich, Martius, Olshausen. Willbrand, Sell, and Geyger.

When the Assistant-Professor, Dr. Blyth, left the College to become Professor at Queen's College, Cork, an old fellow-student of Hofmann's, Sheridan Muspratt, occupied for a short time the post of Honorary Assistant-Professor, and another Giessen student of more recent date, Dr. David S. Price, was also for a time an Honorary Assistant at the College.

There can be no doubt that one of Hofmann's talents which most importantly contributed to his eminence as an industrious and successful investigator, was his faculty of gauging the powers and special qualifications of those who studied under him; it enabled him to select the fittest workers to aid him in the rapid and successful development of a great diversity of researches, and also to direct their special talents and energies into channels which his prolific mind suggested, and the exploration of which, by those whose powers he, in the first instance, discovered and fostered, laid the foundation to the practical usefulness, or the scientific eminence, which many have attained who are now glad and proud to remember that they were the pupils of Hofmann.

A glance at the contents of two volumes published in 1849 and 1853, entitled *Reports of the Royal College of Chemistry and Researches conducted in the Laboratories*, affords interesting illustrations of the manifold directions in which Hofmann guided the students to whom he opened up the inexhaustible fields of original research, and of the fertility of mind which, while he himself was conducting simul-

taneously several investigations, continually branching off into new ramifications, enabled him to suggest a multitude of fresh subjects for work to his students—many of which developed into researches of considerable importance—and to hold the guiding strings of all firmly within his grasp.

Mindful of the importance, to the struggling Institute of which he was the head, of enlisting and maintaining the interest of representatives of professions, industries, commerce, and of landed property, in its work, and of fostering faith in its utility, he encouraged advanced students of a mechanical turn of mind to undertake analyses of waters, soils, ashes of plants, minerals or alloys, or to seek to improve existing, or devise new, analytical methods, or new forms of apparatus; but there is no question that he best loved to place in the hands of his most capable pupils one or other of the many problems in organic chemistry in the solution of which he took a paramount interest. Hofmann's assistants well remember an inseparable pocket companion of his; a small memorandum book, in which he kept a numbered series of subjects for research, and to which additions were frequently made; from these he selected, from time to time, the subject which he placed in the hands of a sufficiently advanced pupil for investigation.

The two volumes to which I have referred record the original papers published during the first five years of the College's existence; they embrace 21 researches in organic chemistry by 19 different pupils, and 15 analytical and other papers in inorganic chemistry by 14 different pupils. But they also include a series of nine of Hofmann's earlier memoirs on the volatile organic bases, besides other researches of much interest conducted by him during those five years of ceaseless activity. In the two or three years following, the number and importance of published memoirs emanating from the College of Chemistry was at any rate maintained, and some valuable technical investigations were, in addition, carried out by Hofmann in conjunction with Professors Graham, Miller, and Redwood.

I have already referred to Hofmann's intimate knowledge of English, even in the first days of his advent here, and of the immediate success which was secured by his lucidity of exposition, even although many of his expressions were at first somewhat literal renderings of his German thoughts. His mastery of the language was extremely rapid, as was testified by the success of two or three most interesting lectures which he delivered to general audiences (subscribers to the College) within two years of his appointment, and by the "Remarks on Experimental Science" and "Introduction to Researches," which constitute the charming and most suggestive prefaces to the first volume of the researches conducted in the laboratory of the College,

and were written between three and four years after his arrival in England. No one could doubt, who saw him and listened to him, when lecturing or taking part in a discussion, that he thoroughly enjoyed public speaking, and no one was followed with closer attention, or with greater interest and enjoyment, than Hofmann when giving the substance of a new research, or taking part in a discussion at this Society's meetings. It cannot be denied that he was somewhat vain of his English; thus, in going through papers prepared by his English students for publication, he did not confine his criticisms to the matter of the treatise, but would not hesitate to alter the language in conformity with his view as to the correctness or appropriateness of expressions or composition. In the preparation of his many memoirs, reports, and addresses he was extremely painstaking, and such truly classical treatises as his discourse "On Ammonia and its Derivatives," published in the *Journal of the Chemical Society* in 1858, and his report on "Chemical Products and Processes," prepared in connection with the International Exhibition of 1862, are monumental illustrations of the thoroughness of his writings. His speeches on festive occasions were a source of much interest to the listeners and of pleasure to himself. The reference to the Exhibition of 1862 recalls to my mind the happy speeches which he delivered in French, German, English, and Italian, when presiding over an entertainment given at Greenwich to the foreign members of the juries, and some there are here present, though, alas! the ranks have been terribly thinned, of his old pupils who will vividly recall to mind that splendid speech in which he bade farewell to them on the occasion of the parting banquet given to him in 1865 by the majority of those who had worked under him at the College of Chemistry.

His famous orations in German, on two recent memorable occasions at Munich and Göttingen, are still fresh in the memory of his many friends here and abroad; but among his many memorable addresses there is one which is invested with a special pathetic interest—the affecting memorial speech which he delivered at the German Chemical Society on the death of his much-loved friend and fellow student, Hermann Kopp, who succumbed to a long and painful illness but a few weeks before Hofmann was so suddenly called away.

Hofmann's life should, and must, have been a very happy one, even although it was often clouded by domestic calamity. He attained to honours and dignity which were tokens of full official and public recognition of his high merits and of valuable services rendered to science and the State. Ample resources and a vigorous constitution enabled him to devote to the great pursuit of his life—research—the little leisure his professorial, literary, and official duties left him. Moreover, he possessed in the highest degree the faculty of making

friends. To be his pupil was to become attached to him—the patient teacher, the enthusiastic worker, the cheering and brilliant companion, to whom it was a pride and pleasure to render service; he readily made and bound to himself powerful and influential friends, and was cordially welcomed wherever he went. He was treated with much kindness by the Queen, and by the Prince Consort who paid repeated visits to the laboratories of the College of Chemistry; he several times delivered lectures at Windsor Castle. Upon his appointment at Berlin he was at once most graciously received by the then Crown Princess of Prussia, the Empress Frederick of Germany, who recently spoke to me of her great sorrow at the death of her dear master and friend, as she called him, and of her high admiration of his talents and character.

The ease with which Hofmann made friends at the very outset of his London career, and the rapidity with which he adapted himself to English customs and mode of life, combined to speedily make him thoroughly at home here, and strongly attached to England and the English. Even after his return to Germany he was fond of speaking of England as his adopted country, and I remember in 1849, when replying to my inquiry whether he had enjoyed his summer vacation in Germany, his saying that he never felt thoroughly at home until he once more trod the London pavement.

The following passages from a charmingly worded German letter, addressed by Hofmann to the Prince of Wales, who, as President of the Society of Arts, wrote to him in 1882, congratulating him upon being the recipient of the Albert Medal, illustrate the pleasure with which, whenever occasion offered, he referred to his career in London.

“The gracious words of your Royal Highness carry me back to the most charming period of my youth—to the time when the August Father of your Royal Highness, the ever memorable Prince Consort, exercised a most important influence upon my destiny—as he did upon those of many—by determining the direction of my future life. I shall never cease to be thankful for the fortunate combination of circumstances whereby I was brought into contact with the high-minded Prince, whose active sympathy opened up to me, at a comparatively early period of my life, a sphere of action in the English metropolis, replete with stimulation and instruction, such as never could have been secured to me by my personal exertions.

“Your Royal Highness will therefore appreciate the depth of feeling with which I receive from the hands of the Son, the medal founded in memory of the Father, and the profound emotion with which I gaze upon the faithful reproduction of the noble features of the so-early

departed one, to whom I, in reality, am indebted for the honour now bestowed upon me.

"With the assurance that the Albert Medal and the letter of your Royal Highness which accompanied it will be inherited by my family as an inseparable legacy,

"I am, Sir,

"Your faithful servant,

"A. W. HOFMANN."

I have endeavoured in this notice to present to the Fellows of the Chemical Society some details of interest relating to the foundation and early history of the School of Chemistry with which the name of Hofmann is identified, and to pourtray some characteristics of this eminent chemist, more especially in the capacity of teacher.

With the nature of the multifarious invaluable research work which he has accomplished I have not ventured to deal in any way; the interesting task of reviewing that work is in much abler hands than mine—in the hands of one of Hofmann's most distinguished pupils, of whose achievements he has often spoken and written in glowing terms; whom I envy the splendid work he himself has accomplished and is still pursuing with undiminished ardour; and who, free from the trammels of official life, has been able to keep pace with, and continue intimately concerned in, the rapid strides which chemical science has made since, half a century ago, the cultivation of that science became a branch of national education in this Country through the invaluable combination of circumstances which placed England under a lasting debt of gratitude to August Wilhelm von Hofmann.

The Origin of the Coal-Tar Colour Industry, and the Contributions of Hofmann and his Pupils.

By W. H. PERKIN, Ph.D., D.C.L., F.R.S.

The illustrious man whose lifework we are called on to commemorate, was well known to very many of us, especially those who had the privilege of being his students and assistants. We can all recall the pleasure and interest with which we listened to the lucid and graphic accounts of his researches which he used to bring before the Chemical Society in years gone by; and great was felt to be the loss, not only to us, but also to the country, when he left it for his fatherland: but now we mourn a far greater loss, and one which we realise more and more deeply as we consider the incidents of his remarkable career—a career of such incessant activity and brilliant achievement.

I am charged with a duty which I wish had been placed in more capable hands than mine: to give an account of the rise and progress of the coal-tar colour industry, and its relation to the Hofmann school; and, as being connected with its commencement, I am requested to make the account to a large extent autobiographical—a part of my task which it would have been more agreeable to me to have seen undertaken by others rather than myself.

This industry holds an unique position in the history of chemical industries, as it was entirely the outcome of scientific research. We have to go back to 1825, when Faraday discovered benzene, or, as he then termed it “bicarburetted hydrogen,” for the first investigation which clearly bears upon the subject. Faraday separated the hydrocarbon from the liquid products condensed on compressing the gas obtained from oil. A year later (1826), Unverdorben obtained aniline by the mere distillation of indigo, and called it “crystalline.” Runge afterwards obtained it from coal-tar oil, and having observed that it produced a violet-blue coloration with chloride of lime, called it “kyanol.” It was subsequently obtained from indigo by Fritsche by distilling this colouring matter with caustic alkali. We then come to the important work of Mitscherlich, who obtained the hydrocarbon benzene from a new source, namely, benzoic acid,—whence the name, and produced from this nitrobenzene. Zinin subsequently found that *benzidam*, as he termed it, could be produced by the action of sulphuretted hydrogen in presence of ammonia on an alcoholic solution of nitrobenzene.

This brings us to the commencement of Hofmann’s researches on aniline, a substance which he used sometimes to speak of as his “first love.” In his first published paper he showed that Unverdorben’s crystalline, Runge’s kyanol, Fritsche’s aniline, and Zinin’s benzidam were all the same compound, for which he afterwards selected Fritsche’s name, aniline. Later on, Hofmann and Muspratt prepared toluidine from toluene from tolu balsam.

The work on the separation of aniline from tar was done before the date of Hofmann’s coming to this country, viz., in 1843. After his arrival here in 1845, he continued his researches, and, to realise something of his indomitable perseverance, it is necessary to remember that, until the coal-tar colour industry was established, practically all the aniline he used in his numerous enquiries was procured by the laborious and costly process of distilling indigo with potash.

In 1843, organic chemistry was still in its infancy, and coal-tar naphtha had not yet been investigated. Runge had isolated carbolic acid, pyrrol, kyanol or aniline, and leucol or quinoline. Naphthalene was well known to exist in tar, having been separated by

Garden, as early as 1820. Dumas had discovered paranaphthalene or anthracene, and chrysene and pyrene had been referred to by Laurent, but these were very doubtful compounds. This was about all that was known of the composition of coal-tar at that time. Hofmann showed, in 1845, that benzene must exist in the naphtha, as he found that aniline could be produced from it, but he never separated this hydrocarbon; shortly afterwards, however, he induced his pupil, Charles Mansfield—of whom he always spoke in the highest terms—to undertake the investigation of the liquid hydrocarbons of coal-tar.

On reading over the account of Mansfield's investigation, and bearing in mind that in those days fractional distillation was conducted in old fashioned glass retorts with the thermometer in the liquid, it is impossible not to admire the patience and perseverance he exercised, as well as the systematic and skilful manner in which he worked.

All who have undertaken fractional distillations, even with all our present knowledge and improved apparatus, know how difficult it is to detect and isolate products in a mixture such as coal-tar naphtha. Yet Mansfield obtained benzene in a pure state, and toluene sufficiently so for Hofmann to prepare toluidine from it. He also obtained pseudocumene, and was led to believe in the existence of xylene. In describing his work, he modestly remarks:—

“It has been perhaps the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of: and perhaps to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in.” (*J. Chem. Soc.*, 1849, 1, 246.)

Amongst the enquiries carried on by Hofmann, in the early days of the Royal College of Chemistry, were those classical “researches regarding the molecular constitution of the volatile organic bases,” in which he succeeded in displacing the hydrogen of the NH_2 -group by different alcohol radicles, eventually obtaining also the ammonium compounds. In the first of these (*J. Chem. Soc.*, 3, 1851) he describes ethylaniline (p. 284), and diethylaniline (p. 288), also methylaniline (p. 295). The method used in these researches, of substituting hydrogen in amines by means of the iodides and bromides of the alcohol radicles, and also the substituted anilines which were obtained, although not connected with the foundation of the coal-tar colour industry, have been of great value in its after development. These few references to observations on the early work carried on at the Royal College of Chemistry, for the sake of science *only*, show, in fact, what valuable material was produced for

the coming new industry ; indeed, without the research of Mansfield, it could never have become an industry.

The foregoing brings the work of the Royal College of Chemistry up to near the date when I became a student there, and it will, perhaps, be well if I here refer to my young days, and state how it came to pass that I had the good fortune to study under Hofmann, especially as it will enable me to say a few words in reference to one of his old pupils who has done much for the cause of science.

As long ago as I can remember, the question what pursuit I should follow was constantly before me. Even when very young, I interested myself in several subjects of a mechanical kind, and worked at them to the best of my ability ; and elementary as the experience then gained was, it had a lasting influence upon me. When I was between 12 and 13 years of age, a young friend was good enough to show me some chemical experiments ; amongst these were some on crystallisation, which seemed to me most marvellous phenomena : as a result, my choice was fixed, and it became my desire to be a chemist, if possible, as I saw that there was in this science something far beyond the mechanical and other pursuits I had been previously occupied with. At this time I left the school I was attending, and entered the City of London School, of which Dr. Mortimer was then head master. Here lectures were given on chemistry and natural philosophy ; indeed, I believe this was the first school in which experimental science was taught. The lecturer was one of the masters, Mr. Thomas Hall, B.A. (Lond.), an old student of Hofmann's, who had obtained all the chemical knowledge he possessed by working at the Royal College of Chemistry. To attend these lectures was a source of great pleasure to me. There was also a yearly examination in science, and the examiner was also one of Hofmann's pupils, and his first assistant, none other than my friend Mr., now Sir, Frederick Abel. In the City of London School I was consequently brought directly under Hofmannic influence, if I may so term it, for all who came in contact with those who worked with him had infused into them by induction his enthusiasm for chemistry. Mr. Hall very soon took an interest in me, and installed me as one of his lecture assistants. Science, however, was not allowed to interfere with the ordinary school curriculum, so that the lectures, and the preparations for them, were delegated to the interval for dinner, and being very much interested in preparing the experiments, I not unfrequently found this interval had passed before I had left off work ; but, fortunately, I never found that the abstinence thus caused acted prejudicially upon me. Whilst with Mr. Hall, I heard much of the Royal College of Chemistry and its Professor, and after my master had very kindly had several interviews with my father—who wished me to be an architect and not a

chemist—it was my good fortune to be allowed to follow my bent, and go to the Royal College of Chemistry, in Oxford Street.

Before passing from my schooldays, I feel I must say a few more words about my old school-master, to whose kindness I owe so much. Thomas Hall was a born teacher, who took an individual interest in his scholars, studying their characters, and stimulating any special qualities he saw they possessed, and, at the same time, inculcating the highest moral qualities. He hated anything that was mean or underhand, and, at the same time, was very genial and kind-hearted; this may be gathered from the fact that the boys used to speak of him as *Tommy Hall*. His influence on behalf of science, especially the science of chemistry, was great; it appears, from a list of old City of London School boys, kindly given me by Mr. John Spiller, that more than 30 boys in whom he had taken an interest afterwards worked at the Royal College of Chemistry, and of these I may mention the following as having contributed papers to our Transactions:

J. J. Bowrey, J. T. Brown, Frank Clowes, W. H. Deering, Edward Divers, J. A. Newlands, F. J. M. Page, W. H. Perkin, Alexander Pedler, J. Spiller, and W. Thorp.

I entered the Royal College of Chemistry when I was in my fifteenth year, at the time when that institution became part of the School of Mines, but I only took up the study of chemistry. After seeing Dr. Hofmann with my father, the first person I encountered in the laboratory was the Assistant, Mr. W. Crookes, who set me to study the reactions of the metals.

There was no theatre at the Royal College then, and the students had to go to the Museum of Practical Geology in Jermyn Street to hear the lectures on chemistry, which involved a rather serious loss of time; but the lectures made up for this, as Hofmann spared no pains in making them as interesting, instructive, and perfect as he possibly could, illustrating, as far as practicable, everything by experiment, so that the facts were firmly impressed upon the mind. At that time he also had a very efficient lecture assistant, the late Mr. Witt. Hofmann was good enough to let me attend these lectures a second time.

When going through the ordinary course of qualitative and quantitative analysis, the students working at research appeared to me to be superior beings, something beyond ordinary persons; and being possessed with a desire to join their ranks, the ordinary course, and also gas analysis by Bunsen's method, was quickly gone through. Hofmann then set me to work at research, and very curiously gave me as a subject the hydrocarbon anthracene, or, as it was generally called in those days, paranaphthalene. To obtain this, pitch was taken as the starting point, but as it was found that this method of

preparation was a very tedious one to carry out in the laboratory, Hofmann kindly obtained some of the crude product for me from Mr. Cliff, of Bethels Tar Works. As is well known, Hofmann—especially at that period—was much interested in the formation of organic bases from hydrocarbons, and the object of my investigation was to produce, if possible, a nitro-compound, and then convert this into a base by reduction. However, anthracene refused to give a nitro-compound, and consequently no base could be obtained, but, in the course of my work, I prepared the compound we now know as anthraquinone, and also the chlorine and bromine derivatives of anthracene. But these substances could not be got to yield intelligible results on analysis, and at that time it never occurred either to Hofmann or myself that there was any likelihood of Dumas and Laurent's formulæ for the hydrocarbon (*i.e.*, $C_{15}H_{12}$) being incorrect. The consequence was that this research was set aside, but I shall show further on that the experience I then gained was of great importance to me several years later, when I commenced to work at the production of alizarin.

Hofmann next set me to work to study the action of chloride of cyanogen on naphthylamine in the same way that he had examined the action of this gas on aniline. In those days there were no dépôts where pure products for research could be obtained as there now are, and for this inquiry even the naphthalene had to be purified in the laboratory; this research was soon completed, but was not written out and published until nearly 12 months afterwards. It was brought before this Society when the meetings were held in Mr. Pepper's house in Cavendish Square.

Hofmann had a marvellous power of stimulating his students, and of imparting to them his own enthusiasm; he took the strongest personal interest in their work, visiting three or four times in the week even those who were going through the reactions, while those engaged in research work were seen daily by him, and if anything of special interest was going on, more than once in the day. His power of directing research was also most remarkable; with the aid of a few watch glasses, a glass rod, and a small gas flame he would make a number of experiments, and from the information thus gained tell his students how to proceed with their work. I well remember how one day, when the work was going on very satisfactorily with most of us and several new products had been obtained, he came up and commenced examining a product of the nitration of phenol one of the students had obtained by steam distillation; taking a little of the substance in a watch glass, he treated it with caustic alkali, and at once obtained a beautiful scarlet salt of what we now know to be orthonitrophenol. Several of us were standing by at the time, and,

looking up at us in his characteristic and enthusiastic way, he at once exclaimed, "Gentlemen, new bodies are *floating* in the air." I mention this just as an example of the way in which he used to stimulate us by his own example.

After I had completed the research on the action of chloride of cyanogen on naphthylamine, Hofmann promoted me to the position of an assistant in his research laboratory; I was then 17 years of age. Mr. A. H. Church, now Professor Church, was among the assistants in the laboratory. This position proved most valuable to me.

At this time Professor Cahours came over from Paris to work with Hofmann on the allyl compounds, a research in which Professor Church and I had to assist. They then commenced their splendid work on the phosphorus bases, and I well remember the excitement and interest which prevailed when Paul Thénard's triethylphosphine was first produced by the action of zinc ethyl on phosphorus trichloride, and Hofmann's delight when he found it was vigorously acted on by methyl and also ethyl iodide, producing white, crystalline, phosphonium iodides. I was occupied with this research until I left the Royal College.

I may here refer to an incident which shows how greatly Hofmann was interested in his scientific work. One day, when he was going his usual rounds in the general laboratory, a student standing not far from him poured a quantity of concentrated sulphuric acid into a thick glass bottle he was holding in his hand, which contained a small quantity of water; the consequence was that the heat evolved caused it to crack and the bottom to fall out. Some of the acid splashed up from the floor into Hofmann's eye, and we feared would have a permanently injurious effect upon it. Hofmann was sent home in a cab, and had to be kept in bed in a dark room during several weeks, his old friend, Dr. Bence Jones, attending him. But during this time, and notwithstanding his sufferings, he was so anxious about his work that we used to have to visit him in his darkened bedroom, to report progress and also to receive any instructions he had to give.

Whilst in the research laboratory I had the privilege of meeting St. Claire Deville, who came to London for the purpose of exhibiting specimens of sodium and aluminium at a lecture given by the Rev. T. Barlow at the Royal Institution, of which the lecturer was Secretary.

Whilst assistant under Hofmann, I had but little time for private work in the daytime; as, however, I wished to continue research work, part of a room at home was fitted up as a rough laboratory, and there I was able to work in the evenings or during vacations.

In this laboratory a research was carried on conjointly with Mr. Church on some colouring matters derived from dinitrobenzene and dinitronaphthalene. One of the products we then obtained afterwards proved to be amidoazonaphthalene, or, as we called it, azodinaphthyl-diamine. This appears to have been the first case of a definite compound being obtained of the azo-class and shown to possess dyeing powers. As Dr. Caro has referred to this in his notice in the *Berichte* of the late Peter Griess, I need not make any further observations on the subject here (*Ber.*, 1892, 25, 4, 1011).

At this period much interest was taken in the artificial formation of natural organic substances; but at the time I was at the Royal College of Chemistry, although the theory of compound radicles, the doctrine of substitution, &c., were occupying much attention, very little was known of the internal structure of compounds and the conceptions as to the method by which one compound might be formed from another was necessarily very crude.

Thus, in the Report of the Royal College of Chemistry, published in 1849, Hofmann refers to the artificial formation of quinine as a great desideratum, and then states

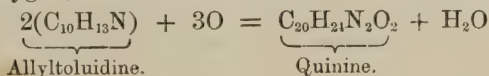
"It is a remarkable fact that naphthalene, the beautiful hydrocarbon of which immense quantities are annually produced in the manufacture of coal gas, when subjected to a series of chemical processes, may be converted into a crystalline alkaloid. This substance, which has received the name of naphthalidine, contains 20 equivalents of carbon, 9 equivalents of hydrogen, and 1 equivalent of nitrogen." (C = 6. O = 8.)

* * * * *

"Now if we take 20 equivalents of carbon, 11 equivalents of hydrogen, 1 equivalent of nitrogen, and 2 equivalents of oxygen, as the composition of quinine, it will be obvious that naphthalidine, differing only by the elements of two equivalents of water, might pass into the former alkaloid simply by an assumption of water. We cannot, of course, expect to induce the water to enter merely by placing it in contact, but a happy experiment may attain this end by the discovery of an appropriate metamorphic process."

In fact there was but little other ground to work upon in many instances than this kind of speculation.

As a young chemist I was ambitious enough to wish to work on this subject of the artificial formation of natural organic compounds. Probably from reading the above remarks on the importance of forming quinine, I began to think how it might be accomplished, and was led by the then popular additive and subtractive method to the idea that it might be formed from toluidine by first adding to its composition C_3H_4 by substituting allyl for hydrogen, thus forming allyltoluidine, and then removing two hydrogen atoms and adding 2 atoms of oxygen, thus



The allyltoluidine having been prepared by the action of allyl iodide on toluidine, was converted into a salt and treated with potassium dichromate; no quinine was formed, but only a dirty reddish-brown precipitate. Unpromising though this result was, I was interested in the action, and thought it desirable to treat a more simple base in the same manner. Aniline was selected, and its sulphate was treated with potassium dichromate; in this instance a black precipitate was obtained, and, on examination, this precipitate was found to contain the colouring matter since so well known as *aniline purple* or *mauve*, and by a number of other names. All these experiments were made during the Easter vacation of 1856 in my rough laboratory at home. Very soon after the discovery of this colouring matter, I found that it had the properties of a dye, and that it resisted the action of light remarkably well.

After the vacation, experiments were continued in the evenings when I had returned from the Royal College of Chemistry, and combustions were made of the colouring matter. I showed it to my friend Church, with whom I had been working, on his visiting my laboratory, and who, from his artistic tastes, had a great interest in colouring matters, and he thought it might be valuable and encouraged me to continue to work upon it; but its evident costliness and the difficulties of preparing aniline on the large scale, made the probability of its proving of practical value appear very doubtful. Through a friend, I then got an introduction to Messrs. Pullar, of Perth, and sent them some specimens of dyed silk. On June 12, 1856. I received the following reply:—

“If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time. This colour is one which has been very much wanted in all classes of goods, and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you pattern of the *best* lilac we have on cotton—it is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests that yours does, and fades by exposure to air. On silk the colour has always been fugitive: it is done with cudbear or archil, and then blued to shade.”

This somewhat lengthy extract is quoted because it gives a glimpse at the state of the dyeing trade in reference to this shade of colour at that period.

This first report was very satisfactory; the “if” with which it commenced was, however, a doubtful point.

During the summer vacation, however, the preparation of the colouring matter on a very small, technical scale was undertaken, my brother (the late T. D. Perkin) assisting me in the operations, and, after preparing a few ounces of product, the results were thought sufficiently promising to make it desirable to patent the

process for the preparation of this colouring matter. This was done on August 26, 1856 (Patent No. 1984). A visit was then made to Messrs. Pullar's, and experiments on cotton dyeing were made, but, as no suitable mordants were known for this colouring matter, only the pale shades of colour, produced by the natural affinity of the dye for the vegetable fibre, were obtained; these, however, were admired. Experiments on calico printing were also made at some print works, but fears were entertained that it would be too dear, and, although it proved to be one of the most serviceable colours as regards fastness, yet the printers were not satisfied with it because it would not resist the action of chloride of lime like madder purple.

Although the results were not so encouraging as could be wished, I was persuaded of the importance of the colouring matter, and the result was that, in October, I sought an interview with my old master, Hofmann, and told him of the discovery of this dye, showing him patterns dyed with it, at the same time saying that as I was going to undertake its manufacture, I was sorry that I should have to leave the Royal College of Chemistry. At this he appeared much annoyed, and spoke in a very discouraging manner, making me feel that perhaps I might be taking a false step which might ruin my future prospects. I have sometimes thought that, appreciating the difficulties of producing such compounds as aniline and this colouring matter on the large scale, Hofmann perhaps anticipated that the undertaking would be a failure, and was sorry to think that I should be so foolish as to leave my scientific work for such an object, especially as I was then but a lad of 18 years of age; and I must confess that one of my great fears on entering into technical work was that it might prevent my continuing research work, but I determined that, as far as possible, this should not be the case.

Still, having faith in the results I had obtained, I left the College of Chemistry and continued my experiments, and found that not only aniline, but also toluidine, xyloidine, and cumidine gave a purple colouring matter when oxidised.

The following is a copy of the principal part of the complete specification of the patent I took out at this time:—

“ Dyeing Fabrics.

“ The nature of my invention consists in producing a new colouring matter for dyeing with a lilac or purple colour stuffs or silk, cotton, wool, and other materials in the manner following:—

“ I take a cold solution of sulphate of aniline, or a cold solution of sulphate of toluidine, or a cold solution of sulphate of xyloidine, or a cold solution of sulphate of cumidine, or a mixture of any one of such solutions with any others or other of them, and as much of a cold solution of a soluble bichromate as contains base enough to convert the sulphuric acid in any of the above-mentioned solutions into

a neutral sulphate. I then mix the solutions and allow them to stand for 10 or 12 hours, when the mixture will consist of a black powder and a solution of a neutral sulphate. I then throw this mixture upon a fine filter, and wash it with water till free from the neutral sulphate. I then dry the substance thus obtained at a temperature of 100° C., or 212° F., and digest it repeatedly with coal-tar naphtha, until it is free from a brown substance which is extracted by the naphtha. Any other substance than coal-tar naphtha may be used in which the brown substance is soluble and the colouring matter is not soluble. I then free the residue from the naphtha by evaporation, and digest it with methylated spirit, or any other liquid in which the colouring matter is soluble, which dissolves out the new colouring matter. I then separate the methylated spirit from the colouring matter by distillation, at a temperature of 100° C. or 212° F."

Fresh quantities of colouring matter were prepared and taken to Scotland, and, although the method of applying it by means of lacterine (casein) was then found to give very good results, yet the printers who tried it did not show any great enthusiasm; and even Messrs. Pullar began to fluctuate in their opinion as to the advisability of erecting plant for its manufacture, and wrote:—"Should it appear that it will not be of service to printers, it will be questionable whether it would be wise to erect works for the quantity dyers alone will require." In January, 1867, Mr. R. Pullar, however, advised me to see Mr. Thos. Keith, a silk dyer of Bethnal Green, London, and, after making a few experiments with the colouring matter, and exposing the specimens he dyed to the light for some time, he was much pleased with the result, and encouraged me to go on with its production.

I was then joined in the undertaking by my father—who was a builder, and had sufficient faith in the project to risk the necessary capital—and also by my brother, who also had a good knowledge of building, and, as he had taken part in the preliminary experiments on the preparation of the dye, his assistance proved most valuable, especially as he was possessed of good business capabilities. Plans were prepared and a site obtained at Greenford Green, near Harrow, and in June, 1857, the building of the works was commenced.

At this time, neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be, as the kind of apparatus required and the character of the operations to be performed were so entirely different from any in use that there was but little to copy from.

In commencing this manufacture, it was absolutely necessary to proceed tentatively, as most of the operations required new kinds of apparatus to be devised and tried before more could be ordered to carry out the work on any scale.

But the mechanical were not the only difficulties. Benzene at this

time was only made to a very limited extent, as there was but little use for it, and it was only after making several inquiries that it was ascertained where it could be obtained. That used at first came from Messrs. Miller and Co., of Glasgow. It was also of very unequal quality, and required refractionating before use; its price was 5s. per gallon. No nitric acid sufficiently strong for the preparation of nitrobenzene could be obtained commercially, and, as we did not want to complicate our works by manufacturing the substance, experiments were made with a mixture of sodium nitrate and sulphuric acid, using the latter in rather larger proportions than necessary to give an acid sodium sulphate. This method was found to succeed on the small scale, but, when working with large quantities, special apparatus had to be devised, and a great many precautions had to be taken to regulate the operation; however, very large quantities of nitrobenzene were made by it. Nitrobenzene had never been prepared in iron vessels before this time.

It was only three years before the works were started that Bechamp had made the interesting discovery that finely divided iron and acetic acid were capable of converting nitrobenzene into aniline; had it not been for this discovery, the coal-tar colour industry could not have been started. To carry this process out on the large scale, special apparatus was also required, and, on account of the energy of the action which takes place, special precautions had to be adopted; but no great difficulties were encountered in this operation. Potassium bichromate at that date fluctuated between 9 $\frac{3}{4}$ d. and 11d. per lb., and was therefore a costly product.

Many more details might be gone into in reference to the difficulties to be contended against at the starting of the industry, but sufficient has been said to give some idea of them; however, in less than six months after the building of the works was commenced, namely, in December, 1857, aniline purple, or Tyrian purple, as it at first was called, was in use for silk dyeing in Mr. Keith's dye-house.

But in dyeing large quantities of silk, difficulties were again encountered, on account of the great affinity of the colouring matter for the fibre causing unevenness, and some time was taken up in experimenting on this subject, until eventually it was found that by dyeing in a soap bath a very pure and even colour could be produced. This process was afterwards found to be the most suitable for dyeing silk with magenta, Hofmann's violet, and many other colouring matters.

Aniline purple having now been proved to be an important colouring matter, which could be produced on a manufacturing scale, it attracted much attention, and, as a consequence, many others com-

menced its manufacture, and also to experiment with aniline, especially in France; all kinds of oxidising agents were used, but potassium dichromate still proved to be the best, the next best being chloride of copper, the use of which was patented by Dale and Caro, in 1860.

The French manufacturers were not long before they succeeded in producing the colouring matter (the French patent being invalid, owing to a mistake as to the date it was necessary to take it out in reference to that of the English patent), and in using it in dyeing their goods, both silk and cotton. The calico printers of this country then began to be alive to the necessity of following them, and this made the demand for the aniline purple—which the French now began to call mauve—so great that, notwithstanding the continued increase which had been taking place in the works at Greenford Green, it could not be kept pace with. At this time, a very beautiful archil colour had been produced by Messrs. Guinon, Marnas, and Bonney, called French purple; this also was applied to calico printing, and the printers in this country who could not get a supply of aniline purple used this until their requirements could be met. A little before this, Mr. Pullar and I separately discovered a process for mordanting cotton, so that it could be dyed with aniline purple to any depth of colour, and thus it became of much more value to the cotton dyer than it was so long as its natural affinity for the fibre could alone be relied upon. The process consisted in the use of tannin and a metallic oxide.

For calico printing, the colouring matter was first applied in combination with lacterin, albumin, or gluten, but endeavours were soon made to find some new method by which these might be dispensed with, and I worked for some considerable time on this subject at the Dalmonach Print Works, Alexandria, Dumbartonshire, where the colour was first practically used for printing in this country. I devised a process, which consisted in printing on a lead salt, converting this into a salt containing a fatty acid by means of soap, and then dyeing in a soap bath containing the colouring matter; the fatty lead salt then took up the colouring matter, whilst the soap prevented the white from being stained; this process was patented by myself and Mr. Mathew Grey. It produced beautiful shades of colour, but could not be used where combinations with other colours were required, and therefore did not prove useful.

Printers then experimented on the use of tannin and a metallic oxide, the process used in cotton dyeing devised by Mr. Pullar and myself; a modified form of this process has become the most important used. Another process was also very largely used, patented by M. Schultz and myself, which consisted in forming an

insoluble arsenite of alumina and colouring matter on the fibre, the colours produced in this way being very brilliant, as well as fast to washing. Before the aniline purple could be introduced for dyeing woollen and mixed fabrics, some weeks were also spent at Bradford in finding out suitable methods of applying it.

Thus it will be seen that, in the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but, owing to the fact that it belonged to a new class of dyes, a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, &c. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all the colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, &c.

All this time a host of experimentalists continued making trials with aniline and all kinds of chemicals, and early in 1859, three years after the discovery of aniline purple, or mauve, M. Verquin discovered fuchsine, also called magenta and roseine, and, later on, rosaniline by Hofmann.

From what has been said above, it will be seen that the discovery of this colouring matter was made under more favourable auspices than that of mauve: everything was ready for its production and application, it was also an easier product to manufacture and relatively to the aniline used was formed in much larger quantities than mauve was, but it was not nearly so fast against light, and when first experimented with I thought this would have been very detrimental to its extensive use, remembering the experience that I had gone through with mauve; but things had changed, and the love of brilliancy had begun to outrun the regard for durability, indeed, as is well known, magenta has proved to be one of the most successful of the coal-tar colours ever discovered. M. Verquin's process was a very remarkable one, and it has never transpired whether he was led to it by any scientific reasoning or not; it will be remembered that it consists in heating commercial aniline and anhydrous tetrachloride of tin nearly up to the boiling point of the mixture; it was first carried out by Messrs. Reynard Bros., of Lyons.

We were thus indebted to France for the second step in the coal-tar colour industry. Soon other processes were invented for the production of magenta, but the most practical one, after M. Verquin's, was that in which mercury nitrate was used; large quantities of colouring matter were made by this method.

The fuchsine, or magenta, first made in France, was but very imperfectly purified, and a good deal of that afterwards made in

Germany simply consisted of the "melt" produced by heating aniline with mercury nitrate.

Being naturally interested in this new colouring matter, I made many experiments with it, and in a lecture I delivered before this Society, on May 16, 1861 (*J. Chem. Soc.*, 1862, **14**, 230) (when I was honoured by the presence of Michael Faraday), an account of some of the results obtained by its examination was given, in which it was shown that it was the salt of an organic base (a fact at that time believed in by some, but doubted by others) precipitated by alkalis and at the same time dissolved by them to some extent, yielding colourless solutions, and that its nitrate could be obtained in the form of octahedrons, having a beautiful green metallic reflection; this was the first occasion, I believe, on which it was described as a crystalline compound. Attention was also called to the fact that its salts could not contain oxygen, which was afterwards confirmed by Hofmann; and it was further pointed out that other products were formed along with it, one possessing an orange colour (chrysaniline), and another a purple colour (violaniline, mauve aniline, &c.).

In speaking of the manufacture of rosaniline in this country, I must first refer to another of Hofmann's pupils, Edward Chambers Nicholson, of the firm of Simpson, Maule and Nicholson, who brought the manufacture of this compound to a state of perfection, which, I believe, has not been surpassed—so far as purity is concerned—up to the present time.

It is of interest to trace the manner in which Messrs. Simpson, Maule and Nicholson, became connected with the coal-tar colour industry. They were originally manufacturers of fine chemicals, &c. When aniline purple was found to be successful, and was exciting a great deal of interest, this and other firms were anxious to manufacture it, and consequently wished to have a licence for the purpose, but no agreement could be come to. They were then very desirous of manufacturing nitrobenzene for our use in producing aniline. At first they could not do this at a sufficiently low price, but eventually succeeded in producing it cheaply enough to make it worth our while to supplement our own make by theirs, as the demand for aniline purple was then so rapidly increasing. In this way they soon became considerable producers of nitrobenzene; they then set to work to prepare aniline, which after a time they succeeded in doing. In this manner they leisurely, as it were, became fully prepared to go a step further, and become manufacturers of colouring matters.

Dr. David Price at this time joined the firm, and Nicholson and he apparently experimented with the products he had patented in 1859, namely violin, purpurin, and roseine, obtained by oxidising aniline with lead peroxide; these colouring matters, however, were not found

to be of practical value. They then turned their attention to the newly discovered colouring matter, fuchsine. This they commenced manufacturing, giving it the name of one of Dr. Price's products "roseine."

H. Medlock, another of Hofmann's pupils at the Royal College of Chemistry, took out a patent on January 18, 1860, for the production of magenta, by heating aniline with arsenic acid; eight days later, Nicholson filed a similar patent, but did not proceed with it when he learnt what Medlock had done. Medlock's patent is notorious for the amount of litigation that arose owing to the occurrence in it of the word "anhydrous." The formation of magenta by the use of arsenic acid proved in the hands of Nicholson, and also of others, a great improvement on the previous processes, and for a long time was *the* process for the production of this colouring matter, until, in fact, it was superseded by the use of nitrobenzene instead of arsenic acid.

One of the things Hofmann used to impress on those of his students who were engaged at research work was the great importance of preparing their products in as nearly pure a condition as possible—especially those which were to be submitted to analysis; some of us used to think that we should get as good results by examining the substances when crystallised fewer times than he required, especially when the products were difficult to obtain and the quantities became smaller and smaller on each recrystallisation; but he was right. Nicholson, when at the Royal College, made several investigations under Hofmann's direction, studying the compounds of phosphoric acid with aniline; the formation of cumidine from cumene from cuminic acid; also caffeine and some of its compounds; and, in conjunction with F. A. Abel, he investigated strychnine. He also appears to have been an adept at combustions, as he made the combustion of benzene for Mansfield; his name appearing also in de la Rue's paper on cochineal as having made one of the combustions of nitrococcusic acid. There is no doubt that Hofmann's teaching as to the importance of working with pure materials was strongly impressed upon Nicholson when carrying on these researches, and that it greatly influenced him when he became engaged in the manufacture of colouring matters. It is only right to add that Dr. D. Price, with whom he was for some time associated in this industry, and whom I knew when at the Royal College of Chemistry as a most thorough, painstaking, and careful worker, would also second his efforts in this respect. I may also add that I feel sure Hofmann's influence in this direction had also a considerable influence on my own after career as a chemist.

At first Messrs. Simpson, Maule, and Nicholson supplied magenta, or

roseine, as they called it, to the dyers in alcoholic solution, but afterwards, when they had obtained it in a pure condition, they sold it in crystals (usually the oxalate). In their process of purification they boiled the crude solution of the colouring matter with milk of lime, and collected the base which deposited from the clear solution thus obtained, and from this prepared the desired salts.

By this time the coal-tar colour industry had become one of no mean dimensions in this country, and also in France, and it was quickly developing in Germany and elsewhere. The number of colours was also increasing, for not only had mauve or aniline purple and fuchsine been discovered, but Gerard and Delaire had made their remarkable discovery of *Imperial violet* and *Blue de Lyon* by heating aniline with fuchsine, thereby—as is now known—*phenylating* this colouring matter.

When first speaking of fuchsine, I mentioned that it was discovered by M. Verquin, and, from a practical point of view, this may be considered correct. Nevertheless it appears to have been first seen as far back as 1856, when Natanson (*Annalen der Chemie und Pharmacie*, 1856, 98, 297) observed that in heating aniline and chloride of ethylene in a sealed tube to 200°, the mixture becomes of a rich blood-red colour; Hofmann also, in 1858, when acting on aniline with carbon tetrachloride obtained, besides carbotriphenyl-triamine, a small quantity of this substance as a secondary product, which he describes as “a very soluble substance of a magnificent crimson colour.” *

In the Report of the Exhibition of 1862 (Class II, sec. A, p. 126), Hofmann, in speaking of the discovery of this colouring matter, says:—“It may be said to have been discovered at two different times according as the question is considered from a scientific or industrial point of view;” and at p. 126:—“Industrially, the discovery of aniline red was made by Messrs. Verquin and Renard Brothers of Lyons.”

The investigation Hofmann made with the Nicholson products soon set at rest the conflicting views which at first existed in reference to this colouring matter, and proved that it was a well defined triamine—which he re-named *rosaniline*—forming salts free from oxygen. He then regarded the base, which had the formula $C_{20}H_{21}N_3O$, as a

* About two years after M. Verquin's discovery of fuchsine, the use of carbon tetrachloride and aniline as a means of preparing this colouring matter was tried, for reasons connected with patent rights, by MM. Monnet and Drury of Lyons. They first employed a temperature of 116—118° until the reaction between these two substances was over, and then heated the product up to 170° or 180°. By this means of working, they apparently obtained a larger yield than Hofmann, but the process never became a practical one. See *Moniteur Scientifique*, T. III, 15 Jan., 1861.

hydrate of the anhydrous compound $C_{20}H_{19}N_3$. Hofmann examined many of the salts of rosaniline—those with one molecule of acid, the ordinary salts used in dyeing, and the hydrochloride with 3 mols. of acid. He also obtained the interesting compound, leucaniline, by treating rosaniline with reducing agents, a compound which has its representation in all triphenylmethane colouring matters. The investigation is a memorable one, as being the first investigation which gave correct information respecting the formula of a coal-tar colouring matter.

It had been observed by manufacturers that some varieties of aniline yield much more rosaniline than others, samples boiling at temperatures much higher than the boiling point of the pure compound being found particularly adapted for the production of the red; and it appears that Nicholson had ascertained that pure aniline was incapable of yielding rosaniline. Hofmann studied this subject, using aniline prepared from indigo and from pure benzene, and his experiments confirmed Nicholson's. The idea then naturally suggested itself, that the toluidine contained in commercial aniline might be the source of the colouring matter. But, on making experiments with toluidine (orthotoluidine was not then known) it was found that this base also was incapable of producing the dye-stuff; on taking a mixture of aniline and toluidine, however, it was at once produced in quantity, showing that both bases were necessary for its production (Report, International Exhibition, 1862, Class II, sec. A, 130).

This discovery was of great importance and interest, and explained most of the facts connected with the use of anilines of different boiling points. In the case of mauveïne, this discovery was not of so great importance as in the case of rosaniline, because pure aniline yields a purple colouring matter (pseudomauveïne), as well as mixtures of aniline and toluidine.

Mauve had also been obtained in a pure crystallised condition, but technically this was not found of much advantage, as the colours obtained with it in this condition were only slightly superior to those obtained with the less expensive precipitated colouring matter which was usually supplied to the consumer.

Having examined aniline red or rosaniline, Hofmann was also desirous of investigating aniline purple or mauve, but when he spoke to me on the subject, the colouring matter was already under investigation in my own laboratory.

The crystallised aniline purple sent into the market was the acetate of the base to which I gave the name mauveïne. This base is remarkable for its stability and tinctorial power. Its investigation (1864, *Proc. Roy. Soc.*, 12, 713) showed that it possesses the formula $C_{27}H_{24}N_4$, and

that, unlike rosaniline, it is not a hydroxy-compound. Moreover, the base is a strongly coloured compound of a blue-violet colour. When treated with reducing agents, it yields a leuco-compound, but this is so sensitive to the action of oxygen that on exposure to the air it instantly changes back to mauveine. Its ordinary salts are produced from 1 mol. of base and 1 mol. of acid. From a more recent research on this colouring matter (*J. Chem. Soc.*, 1879, 717), I have shown that a dihydrochloride and corresponding platinum salt can be obtained, and from the characteristic changes which a solution of this substance, in concentrated sulphuric acid, undergoes on dilution, namely, from a dull green to a blue, and lastly to a purple, shows that probably salts formed by the union of mauveine with more than 2 mols. of acid exist. The ordinary commercial product has also been shown to consist of two colouring matters, one forming very soluble and apparently uncrystallisable salts called pseudomauveine, having the formula $C_{24}H_{20}N_4$, and produced from pure aniline; the other forming less soluble and beautifully crystalline salts of the formula $C_{27}H_{24}N_4$, derived from paratoluidine and aniline. This colouring matter, unlike rosaniline, does not freely undergo changes with reagents on account of its great stability, so that few derivatives have been obtained from it serving to elucidate its constitution, which is still unknown.

Messrs. Simpson, Maule, and Nicholson, after engaging in the manufacture of rosaniline for some time, undertook that of Girard and Delaire's Imperial Violet and Blue de Lyon, obtained by heating a salt of rosaniline with aniline (Pat., January, 1861).

Mr. Nicholson spent much time in studying the conditions most favourable to the production of these compounds, especially the blue, so as to obtain it in a pure condition, and in this he was very successful. This was due to his knowledge of the importance of using pure materials in its manufacture. The rosaniline base he used was not merely the best he produced for the preparation of rosaniline salts, but he purified it much further by means of methylated spirit; the aniline was prepared for the purpose from the purest benzene he could obtain; he also paid much attention to the selection of the best acid to use in combination with rosaniline, and found that weak organic acids, such as acetic and benzoic acids, were the most suitable. In this way he eventually obtained the blue in a condition of purification unequalled by others.

Provided with the purified blue by Nicholson, Hofmann soon discovered that the base had the formula $C_{38}H_{33}N_3O$; this he regarded as a hydrate of the compound $C_{38}H_{31}N_3$, of which he obtained a hydrochloride of the composition $C_{38}H_{31}N_3HCl$. The blue was converted by reducing agents into a leuco-compound.

As far back as 1850 (*Phil. Trans.*, **1**, 93, *J. Chem. Soc.*, **3**, 283), when engaged in his researches on the molecular constitution of the volatile organic bases, Hofmann had endeavoured to displace the hydrogen in aniline by phenyl, by heating it with phenol, but was unsuccessful; we can, therefore, easily understand his delight when he found that on boiling rosaniline with aniline the colouring matter became phenylated. The long desired method of effecting the displacement of hydrogen by phenyl had, in fact, been discovered, and we find that no sooner had he recognised that the blue was a triphenyl rosaniline than he telegraphed the result to Paris.* The *Comptes rendus* of the sitting of the Academy of May 18th, 1863, contains the following note:

"M. Le Secrétaire Perpétuel communique une Courte Note de M. Hofmann conçue dans les terms suivants.

"Bleu d'Aniline.—En poursuivant mes recherches sur les couleurs d'aniline, je suis arrivé à un résultat très simple; le bleu d'aniline est la rosaniline triphénylique: une molécule de rosaniline et trois molécules d'aniline renferment les éléments d'une molécule de bleu d'aniline et trois molécules d'ammoniaque."

The paper, communicating fuller details of his results on this colouring matter, was read on July 6th of the same year (*Compt. rend.*, 1863, **57**, 25). Speaking in this paper of Nicholson, he pays him this tribute: "That in him was united the genius of the manufacturer and the habits of a scientific investigator."

We find the discovery of the phenylation of rosaniline afterwards bearing fresh fruit in the hands of Delaire, Gerard, and Chapoteaut, who established the remarkable fact that when boiled with its own hydrochloride, aniline acted in a similar manner, producing diphenylamine and ammonia; by using aniline hydrochloride and toluidine, they, in like manner, obtained phenyltoluylamine (*Compt. rend.*, 1866, **63**, 91).

Aniline blue having proved to be triphenylrosaniline, it was soon seen that the different shades of violet imperial were rosanilines more or less phenylated.

Nicholson also found that, on heating acetate of rosaniline to 200—215°, ammonia was disengaged, and a purple colouring matter produced, which he called regina purple. This substance was found to be a monophenylrosaniline (patented January 20, 1862).

One of the great obstacles in the way of the application of aniline

* Hofmann had made this discovery apparently on the same day, for Professor LeLeod who was his assistant at that time, gives me an entry from his diary dated May 18th, 1863, which runs thus: "The doctor told me that he had made a fine discovery, and that aniline blue is the triphenylated rosaniline. Rosaniline, $\text{C}_{20}\text{H}_{19}\text{N}_3\text{H}_2\text{O}$; aniline blue, $\text{C}_{20}\text{H}_{16}(\text{C}_6\text{H}_5)_3\text{N}_3\text{H}_2\text{O}$."

blue was its slight solubility in water, which rendered the dyeing operations unsatisfactory; this also militated against its use in calico printing for some time (the most suitable process for its use for this purpose first found being that of Schultz and myself with arsenate of alumina, but with this long steaming and afterwards clearing in a soap bath was required; the colours thus obtained, however, were very pure and very durable). Nicholson naturally was very desirous of overcoming this obstacle, and no doubt the well known process of rendering indigo soluble by dissolving it in sulphuric acid, and then converting it into a sulphonic acid, occurred to him; at any rate, by experimenting in this direction, he succeeded in obtaining the desired result and patented the process (June 1, 1862). Nicholson obtained two sulphonic acids—a mono- and a tri—the first being known as Nicholson's blue, and the latter as soluble blue, and it is owing to the discovery of these derivatives of aniline blue or triphenylrosaniline that this colouring matter became of such importance.

This method of treating aniline blue was very interesting as being the first instance of sulphonating an aniline colour, a process which of late years has become of so much importance, not only in rendering difficultly soluble dyes soluble, but also in changing the chemical nature of the colouring matters, and thus extending their applications as dyes, as in the case of rosanilinesulphonic acid.

It was Nicholson who succeeded in isolating the yellow or orange colouring matter which is formed in the manufacture of rosaniline; he prepared it in a pure state, and called it "phosphine." Hofmann undertook the examination of this dye, and showed that it is represented by the formula $C_{20}H_{17}N_3$, differing from that of rosaniline in containing 2 atoms of hydrogen less; the base is capable of forming salts with 1 or 2 mols. of hydrochloric acid, the nitrate being remarkable for its insolubility.

After discovering that aniline blue or bleu de Lyon was a triphenylrosaniline, Hofmann was very naturally inclined to experiment on rosaniline with the agents he had used so successfully in his experiments on the molecular constitution of the volatile organic bases, namely, the haloid compounds of the alcohol radicles, to see what influence these radicles would have if introduced into the base: he found that they had, like phenyl, though not to the same extent, a blueing effect, the colour changing from red to purple, and then to violet as the hydrogen atoms were gradually displaced, colouring matters being produced which were found to be of great beauty when applied to silk, &c. In his first paper on these products (*Compt. rend.*, 1863, **57**, 30), he gives an account of the action of methyl, ethyl, and amyl iodides on rosaniline, and amongst the products he obtained at that time describes the highest ethylated derivative he

had succeeded in producing as the iodethylate of triethylrosaniline, $C_{20}H_{16}(C_2H_5)_3N_3 \cdot C_2H_5I$.

He patented the method of producing these colouring matters on May 22, 1863.

It is easy to see how Hofmann was led to the production of these compounds in the regular sequence of his work, but it is curious that E. Kopp had evidently prepared some of them as long back as 1861. E. Kopp remarks in his paper in the *Comptes rendus*, 1861, 52, 363, "I have only stated in my notice these substitutions as a hypothesis, but their existence is very real; I have already obtained some of them, and it is a remarkable thing that the red shade disappears, and is converted into a violet, becoming bluer and bluer as the hydrogen is displaced by the hydrocarbons." It appears that he sent some specimens of his products to M. Dumas.

When Hofmann patented the use of methyl, ethyl, and amyl iodides for the preparation of these colouring matters, it seemed almost incredible that substances such as these, which had hitherto only been used in research, should be employed in the manufacture of a dye; but such circumstances have constantly arisen in the history of this remarkable industry—aniline itself, the parent of artificial colours, being an example—and nothing now appears to be too rare or difficult to prepare, to be used in its development.

It is difficult to understand why E. Kopp did not go on with his work on these substitution compounds, unless it was owing to the fact that rosaniline was expensive in his days, and he considered the alcoholic haloids too costly to employ for practical purposes.

The Hofmann violets were the most brilliant in colour of any which had been produced, and proved not to be so costly as might be anticipated, as the iodine from the ethyl iodide used could be mostly recovered; but these colouring matters have not the stability of mauve or imperial violet, and at first it was thought that their use would be limited, but the increasing desire for brilliancy was still superseding that for stability, and the result was, that these colouring matters were very largely used, and interfered very considerably with the sale of the mauve and imperial violets, except for pale shades of colour, when, unless the colouring matter used be stable, the goods fade so quickly as to be of little value.

The products formed on heating mauveïne salts with aniline apparently are not comparable with those obtained from rosaniline, and although the product becomes bluer no ammonia is evolved; from my later experiments, it seems most likely that the aniline used takes no part in the change, the blueing being a change in the colouring matter, the consequence of the temperature employed.

When treated with ethyl iodide, mauveïne behaves unlike rosanil-

ine, yielding a beautiful colouring matter, which is of a *redder* shade, and not bluer as in the latter case. This colouring matter, called *dahlia* (patented on November 6, 1863), consists of a monethylic derivative of mauveïne, its hydrochloride being represented by the formula, $C_{27}H_{23}(C_2H_5)N_4.HCl$. No further change is effected by ethyl iodide, and it is uncertain whether the product is a substitution or an addition compound (it may be remarked here that at times some quantity of a dark, blue-black, almost insoluble substance containing iodine is also produced).

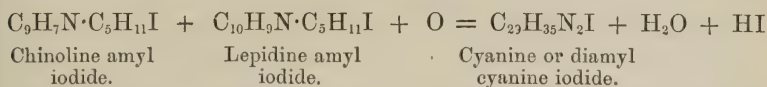
This dahlia or ethylmauveïne was used by the calico printers and dyers to some extent, though not largely, on account of its costliness. It is, however, a colouring matter, which gives shades of very considerable stability on exposure to light.

The discovery that the introduction of such radicles as phenyl or ethyl altered the colour of rosaniline so greatly, made it of interest to see whether other kinds of hydrocarbon groups could be introduced to modify its tint. Amongst other products, brominated turpentine was used, and on heating it with rosaniline hydrochloride dissolved in methylated spirit or methyl alcohol under pressure, it was found that a very beautiful purple or violet colouring matter could be produced; the process was patented in 1864, and large quantities of a colouring matter, known as *Britannia violet*, were prepared in this manner. At first it was thought that the hydrocarbon radicle of the brominated turpentine entered the rosaniline, but it now appears most probable that the product consisted of methylrosanilines produced by the action of methyl bromide formed from hydrogen bromide resulting from the decomposition of the bromo-compound. The colouring matter was more soluble than Hofmann's ethyl violet, but I could not succeed in crystallising it, and, therefore, it was not subjected to analysis.

When the base of Britannia violet is acted on by acetyl chloride, two products are obtained, namely, a violet colouring matter much bluer in shade than the original violet, and a bluish-green compound. The base of this latter has a very feeble affinity for acids, and does not combine with acetic acid, whilst the base of the violet compound does so freely, and in virtue of these different properties the two colouring matters are easily separated. The green dye proved to be of practical value, and considerable quantities of it were prepared for the calico printers, and was known as "Perkins green;" but after a time it was displaced by iodine green. It has not hitherto been investigated. For its manufacture, large quantities of terchloride of phosphorus were prepared, from which and acetic acid large quantities of acetyl chloride were made—another instance of the use of a research reagent on the large scale.

The last investigation relating to colouring matters carried out by Hofmann in this country was that of the very interesting substance known as *chinoline blue*, discovered by Greville Williams, of which the latter gave an account in the *Chemical News* for October 11, 1860 (p. 219). A beautiful specimen of the crystallised substance was displayed in the exhibition of 1862 under the name of *Cyanin*. Chinoline blue was of a very pure shade of colour, and, although an expensive product, attempts were made to introduce it as a dye; unfortunately, although produced from bases of remarkable stability, it was very fugitive, goods dyed with it fading very quickly indeed when exposed to the light—its sensitiveness being so great that on placing it under a glass positive photograph and exposing to sunlight, after only a short time, a chinoline blue positive picture was produced.

Hofmann separated from chinoline two blue compounds, to one of which he gave the formula $C_{30}H_{39}N_2I$, and to the other the formula $C_{28}H_{33}N_2I$. According to later researches, the blue is a condensation product derived from chinoline amyliodide and lepidine amyliodide.



This formula differs from that given by Hofmann to one of the products he examined by an atom of carbon only.

After I left the Royal College of Chemistry, the researches on the phosphorus bases in which I had been helping were continued by Drs. Leibius and Holzmann, to whose able assistance Hofmann refers in one of his papers; but in carrying out the part of this work relating to the phosphammonium, phospharsonium, and arsammmonium compounds, another assistant was active who is referred to by Hofmann in the following words:—

“I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus bases. The truly philosophical spirit in which this talented chemist has accompanied me through the varying fortunes of this inquiry, will always be one of my pleasing recollections.”

We know how the high opinion thus expressed by Hofmann of Griess not only lasted, but became enhanced as time went on; and although Griess was not one of Hofmann's pupils, I cannot refrain from thus referring to him here, as several of his most important early researches on the diazo-compounds were made within the walls of the Royal College of Chemistry, thereby connecting this Institution with work which of late years has had such a marvellous

influence on the development of the coal-tar colour industry. But it is not my intention, nor indeed is it necessary for me, to go into the history of the diazo-compounds, as this has been so very ably done by my friend Caro in his memoir of Peter Griess, whom he held in such high esteem, and who was also one of his greatest friends.

Hofmann's departure was not only a cause of regret to those who had worked under him and to all his friends; it was a heavy loss also to the country at large, as no one had ever done so much for the cause of chemical science in the kingdom as Hofmann did, nor had any one exercised to such an extent that wonderful power he possessed of stimulating the enthusiasm of his students and of inciting in them a love of chemistry and of scientific research. His success is especially striking when the early history of the Royal College of Chemistry is taken into account—especially its financial difficulties, the dissatisfaction of some of the subscribers, and the want of understanding as to the value of scientific research shown both by them and the public at large. When all these circumstances are considered, we cannot but marvel at the courage and indomitable determination he displayed, which enabled him to overcome all difficulties and to persevere in maintaining the high standard of teaching he adopted at the beginning, as well as to continue the prosecution of scientific research for its own sake.

Notwithstanding the immense amount of work Hofmann must have had to attend to in connection with the building and fitting up of the new chemical laboratories of the Frederick William University of Berlin, which took place during the first four years after he left England, namely, from May, 1865, to May, 1869, no break occurred in his scientific activity, each year producing accounts of fresh work accomplished. It was not, however, until 1869 that he published anything fresh in connection with the coal-tar colours, but in this year several communications appeared.

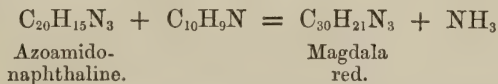
Having found that the production of rosaniline depended on the presence of two bases, aniline and toluidine, he naturally carried his investigation of the subject further, and experimented with xylidine (meta). However, on heating this base with oxidising agents, either alone or in presence of toluidine, no colouring matter was obtained; but when it was heated with pure aniline, a red was formed, which he called xylidine red, which was supposed to be a homologue of rosaniline, probably of the composition $C_{22}H_{25}N_3O$. The colour produced on wool and silk by this dye-stuff was almost as bright as that of rosaniline itself (*Ber.*, 2, 377). In a second paper relating to this subject, published in conjunction with Martius (*Ber.*, 2, 411), an account

is given of similar experiments with an isomer of xyloidine, amidoethylbenzene, which, from the more recent researches of Beilstein and Kuhlberg (*Zeitsch. f. Chem.*, [2], 5, 524), we now know must have been a mixture of the ortho- and para-compounds. No red colouring matter was formed from this on boiling it with an oxidising agent, either alone or mixed with toluidine or even with aniline, thus affording proof of the interesting fact that an ethyl group cannot take the place of a methyl group in the interaction which is involved in the production of colouring matters of the rosaniline class.

After the discovery of mauve and magenta, many experiments were made with α -naphthylamine, as a source of colouring matter, and a variety of products were obtained and patented; but it is unnecessary for me to enter into an account of these here, as most of them were found to be of no technical value. I may, however, allude to two naphthalene derivatives which have proved useful; the first of these, naphthazarin, was discovered by Roussin in 1861, who thought it was artificial alizarin; this beautiful substance, which is now known to be a dihydroxy- β -naphthaquinone, lay dormant for a long time, but, owing to the discovery of improved methods of producing it, has of late come into use for dyeing black on wool. The second was discovered by Martius, and is known as "Martius yellow" or dinitro- α -naphthol. These were the principal colouring matters derived from naphthalene known prior to 1867, when Schiendl discovered the naphthalene red now known by the name of Magdala red, a substance remarkable for the beautiful fluorescence of its solution. The original process for its preparation consisted in heating naphthylamine, acetic acid, and potassium nitrite together, and then adding more naphthylamine and again heating until the desired colouring matter was produced.

Hofmann investigated this red, and assigned to it the formula $C_{30}H_{21}N_3$ (*Ber.*, 1869, 2, 374).

As this colouring matter and the above formula appeared to be related to an old friend of mine, azodinaphthyldiamine (amidoazonaphthalene), I made it the subject of experiments, and found that it was easily produced on heating amidoazonaphthylene with an acid and naphthylamine, an action taking place which it was thought involved the displacement of an atom of hydrogen by naphthyl and the formation of ammonia:



The colouring matter was called azotrinaphthyldiamine (*Proc. Roy. Inst.*, 1869, May 14).

In a second paper, published in July of the same year, on the nature of naphthalene red, Hofmann confirms my observation (*Ber.*, **2**, 413).

It has since been shown, however, by Julius (*Ber.*, 1886, **19**, 1365), that the action which occurs when amidoazonaphthalene is treated with naphthylamine is not nearly so simple as above indicated, and that the formula of the hydrochloride of Magdala red is $C_{30}H_{21}N_4Cl$, not $C_{30}H_{22}N_3Cl$.

The research on Magdala red led Hofmann to study the compound produced by the action of aniline on amidoazobenzene, a substance described by Martius and Griess, but discovered by Dale and Caro in 1863, and called by them *induline*. The examination of this product was afterwards continued by Hofmann in conjunction with Geyger, under the heading of colouring matters obtained from aromatic azo-diamines, and published in 1872 (*Ber.*, **5**, 472). They called this substance azodiphenyl blue, and showed that its hydrochloride had the formula $C_{18}H_{16}N_3Cl$.

In 1869 Hofmann also continued his researches on chrysaniline, studying the action of methyl and ethyl iodide on the base; he obtained trimethyl and triethyl substitution products (*Ber.*, **2**, 378).

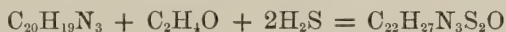
In preparing Hofmann violet, it was found that on precipitating the colouring matter from its aqueous solution by means of sodium chloride, a certain quantity of a bluish-green product remained in solution which could not be separated (though improved in colour) by the addition of sodium carbonate; this was precipitated by means of picric acid, and as it proved to be a valuable green dye, it, after a time, was supplied in small quantities to dyers under the name of iodine green. It was then found by J. Keisser (French patent, April 18, 1866) that the colouring matter could be obtained in much larger quantities by methylating rosaniline, dissolved in methyl alcohol, with methyl iodide, the operation being completed at a comparatively low temperature, and eventually it was obtained in a pure crystallised state. This substance being evidently related to the methylrosanilines, Hofmann was naturally interested in it, and with Girard undertook its investigation (*Ber.*, **2**, 440).

The results they obtained, on analysing the iodo-compound, led them to represent it by the formula
$$\left. \begin{array}{c} C_{20}H_{16} \\ (CH_3)_3 \end{array} \right\} N_3 \left\{ \begin{array}{c} CH_3I \\ CH_3 \cdot I \cdot H_2O \end{array} \right.$$

They found that this compound decomposes when heated at the temperature of boiling water for a few hours, and instantly at 130—150°, becoming changed into a violet colouring matter; in fact, it behaves like an ammonium or addition product. As the complicated history of the methyl and ethyl derivatives developed, it was found that the formula above given required to be modified to some extent; but this is in no way surprising, as it is practically

impossible by analysis alone to arrive at a true conclusion as to the constitution of a compound of such high molecular weight, so unstable and so difficult to obtain pure.

Another green dye-stuff to which Hofmann directed his attention at this time was aldehyde green, produced by the action of aldehyde on rosaniline in presence of sulphuric acid whereby a blue colouring matter is formed, which is transformed into the green by the action of an aqueous solution of sodium thiosulphate. Lauth, apparently, was the first to produce the blue compound, in 1861, by subjecting a solution of rosaniline in alcohol, methyl alcohol, acetic acid, or acetone to the action of zinc chloride and other metallic salts, but the conversion of the blue into the green was accomplished by Cherpin in 1862. This was the first aniline green dye discovered (emeraldine, which was of no value, excepted), and was much used. Hofmann showed that aldehyde green contained sulphur, and assigned to it the composition indicated by the formula $C_{22}H_{27}N_3S_2O$, representing its formation by the following equation,



(*Ber.*, 1870, **3**, 761).

The next researches it will be most convenient to refer to, though not quite the next as to date, are those on the methyl violets; but, before considering these it may be mentioned that, in continuation of his researches on rosaniline derivatives, Hofmann, in 1873 (*Ber.*, **6**, 263), examined the violet obtained by Hobrecker by the action of benzyl chloride and methyl iodide on a solution of rosaniline in methyl alcohol, assigning to it the formula $C_{20}H_{16}(C_7H_7)_3N_3, CH_3I$.

Until long after the commencement of the coal-tar colour industry, chemists and experimenters directed their attention chiefly to aniline as a source of colouring matter; but in 1861 Lauth made some experiments on the product Hofmann obtained by acting with methyl iodide on aniline, which he described as methylaniline (*J. Chem. Soc.*, 1851, **3**, 296), but which recent researches have shown is a mixture of methylaniline and dimethylaniline, and by oxidising this he obtained violet colouring matters. Writing of these in 1867, Lauth says (*Laboratory*, 1867, 138), "The violets obtained from methylaniline possess a richness and purity which leave nothing to be desired Nevertheless, they were not adopted by manufacturers, who, indeed, at the time mentioned (1861) attached less importance to the beauty of a colour than to its permanence. In this latter respect the methylaniline violets do not excel, and, consequently, dyers would have nothing to do with them.

"Gradually, however, people have become accustomed to colours which fade on exposure to the solar rays Accordingly,

two years after the experiment made by myself, Dr. Hofmann succeeded in introducing these results." These remarks confirm those already made in reference to the gradual change in public opinion which led to the disregard of permanency in favour of brilliancy of colour.

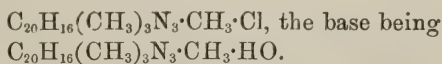
Lauth further remarks that Hofmann's method of producing these colouring matters is the inverse of that proposed by him; the aniline being first converted into rosaniline and then methylated, whilst in his case this operation is first performed on the aniline.

It would, however, not have been practicable to carry out this process if the aniline had to be methylated with methyl iodide, because the base thus prepared would be too expensive to use as the raw material for the preparation of colouring matters. On account of the success of the Hofmann violet, experiments were made in France with the object of preparing methylaniline by a different and more economical process, so as to commercially produce Lauth's violet, and this was at that time considered especially desirable by some manufacturers, because the production of rosaniline in France was the monopoly of one house, and, therefore, derivatives of this colouring matter could not be economically made by others.

Eventually a successful process was discovered by M. Bardy, chemist to the firm of Poirier and Chapat, which consists in heating a mixture of aniline hydrochloride and methyl alcohol in a closed vessel to a high temperature. As is now well known, though not at first recognised, this process yields a mixture of mono- and di-methylaniline, consisting chiefly of the latter. Large quantities of methylated aniline were soon produced by this process, and used in the preparation of a violet colouring matter which was manufactured by Messrs. Poirier and Chapat, and called by them violet de Paris; a large block of this, weighing about 150 kilos, was exhibited in the Paris Exhibition of 1867(?). The question then arose as to whether violet de Paris was identical or isomeric with methylrosaniline violet. Lauth considered that it was isomeric, and remarks: "Hofmann violets consist of methylated and ethylated rosaniline, and rosaniline is derived from a molecule of aniline and two molecules of toluidine. The violet de Paris, on the contrary, is produced from pure aniline free from toluidine, transformed into methylaniline, which is isomeric with toluidine. This methylaniline when oxidised is converted into the violet which may have a composition analogous to that of methylated rosaniline, but must differ from the latter in the same manner as methylaniline differs from toluidine."

Hofmann, being naturally interested in the relationship of these colouring matters, investigated the subject, and published his results

in 1873 (*Ber.*, **6**, 352). He first studied the conditions under which the colouring matter could be formed, showing that violet could be produced from pure dimethylaniline obtained by the distillation of trimethylphenylammonium hydrate; he also came to the conclusion from the examination of the colouring matter that it was a methyl-chlorhydrate of trimethylrosaniline.



He prepared iodine green by methylating this compound; also its leuco-compound.

This research must have been a very difficult and laborious piece of work, and although Hofmann's views as to the constitution of the dimethylaniline violet are not those now accepted, the accuracy of his work has not been impugned.

The long controversy which arose, soon after the time when Hofmann published his constitutional formula of rosaniline, as to the constitution of this colouring matter belongs to another chapter, and need not be referred to here.

Mention has already been made of the process for methylating aniline discovered by Bardy, which consisted in heating this base with hydrochloric acid and methyl alcohol. In 1871 Hofmann and Martius (*Ber.*, **4**, 742) made some experiments in reference to this method, working at higher temperatures than those usually employed (280–300°), and continuing the heating for a considerable time; in this way they obtained, besides methyl and dimethylaniline, a quantity of basic oil of higher boiling point, which eventually proved to be a complex mixture of methylated homologues of dimethylaniline, the products of an intramolecular change or atomic wandering.

These remarkable researches, like so many other purely scientific discoveries, ere many years had passed, were found to be of technical value in connection with the coal-tar colour industry, the cumidine that is so extensively used in the preparation of some of the diazo-colours being made by the method of Hofmann and Martius by heating xylidine with hydrochloric acid and methyl alcohol to a high temperature, about 300°.

Reverting once more to the early days of the coal-tar colour industry, I may now mention that the liquors from which mauve was precipitated were found to contain a red colouring matter which I succeeded in separating, although the amount obtainable was very small. This proved to be a beautiful dye producing crimson-red shades on silk. It was afterwards discovered that it could be produced by the oxidation of mauveine, and it was prepared in considerable quantity in this way, but was a very expensive product, and therefore

not very largely used. This dye-stuff was known first as "aniline pink," and afterwards as "safranine." In 1865 a colouring matter having the properties of safranine was produced without the use of mauveine by F. Duprey, by heating commercial aniline dissolved in acetic acid with lead nitrate. It was then obtained by acting on commercial aniline with nitrous acid and oxidising the mixture with arsenic acid. The colouring matter prepared in this way was examined by Hofmann and Geyger (*Ber.*, 1872, 5, 531). They found it to be a base forming crystalline salts, among others a hydrochloride having the composition $C_{21}H_{21}N_4Cl$. As they found that it could not be produced from either aniline or paratoluidine, or a mixture of the two, but from orthotoluidine, they regarded it as a toluidine derivative. They also observed that the formula above given differs from that of mauveine by C_6H_4 , making it appear possible that mauveine was phenylsafranine. In the course of an investigation of the safranine, obtained by the oxidation of mauveine, of which I published an account some time after this (*J. Chem. Soc.*, 1879, 35, 728), this substance was shown to form a hydrochloride represented by the formula $C_{20}H_{18}N_4$, which differs from that of the substance examined by Hofmann and Geyger by CH_2 . On examining a commercial product manufactured by Messrs. Guinon and Co., of Lyons, from commercial aniline, both substances were found to be present, showing that two "safranines" existed, and I then also showed that probably a third was formed by the oxidation of pseudo-mauveine.

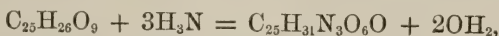
The formula of the safranine hydrochloride obtained from mauveine will be seen from the above to differ from mauveine by C_7H_6 , so that the relationship of these substances is probably not of so simple a character as Hofmann and Geyger supposed, though, of course, C_7H_6 may simply mean displacement of hydrogen by tolyl. No doubt a great similarity exists between them, one proof of which is that their behaviour with sulphuric acid is analogous. This applies both to those referred to above and to the third compound since discovered.

In 1875 Hofmann made an examination of eosin (*Ber.*, 8, 62), and thus disclosed to the world an important manufacturing secret, proving to demonstration the impossibility in these days of long hiding from chemists the nature of any substance, however complex. Eosin, as is well known, was the first representative of a new class of colouring matters which has since become of great importance.

Chrysoidine, which may fairly be termed the parent of an even more important class of colouring matters, the azo-dyes, the introduction of which marks a new era in this branch of chemistry, was investigated and publicly proclaimed by Hofmann in 1877 (*Ber.*, 10, 213).

The colouring matter to which he next directed his attention was

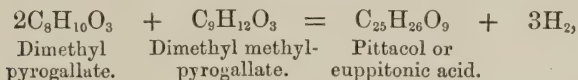
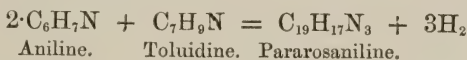
pittacal, also called euppitonic acid, the interesting compound discovered by Reichenbach, as far back as 1835, produced from wood tar. Hofmann (*Ber.*, 1878, **11**, 1655; 1879, **12**, 1371 and 2216) was led to regard this substance as hexamethoxyrosolic acid, $C_{19}H_8(OCH_3)_6O_3$; on treating it with ammonia, he obtained a beautiful blue dye-stuff, thus,



which he regarded as hexamethoxypararosaniline,



He then made the interesting discovery that the formation of pittacal, or euppitonic acid, from dimethylpyrogallate and dimethylmethylpyrogallate took place in a manner analogous to that in which pararosaniline was formed, thus,



comparisons which are of considerable interest.

Hofmann's last research in connection with the coal-tar colour industry was made as late as 1887, and related to the quinoline red prepared by Jacobson, in 1882, from coal-tar chinoline, benzotrichloride, and zinc chloride. Hofmann, however, found that a better yield of colouring matter, either identical or isomeric with Jacobson's, is obtained by using a mixture of isoquinoline and quinaldine. Like quinoline blue or cyanine, the colour is not a fast one, which, as previously mentioned, is remarkable, considering the stability of quinoline itself. It is a somewhat remarkable coincidence that this should have been the last research Hofmann made on the coal-tar colours, as chinoline (or leucoline) was one of the two substances he gave an account of in his first investigation published in 1843, when 30 years of age.

Excepting what is said of pittacal, and the brief reference to eosin and chrysoidine, the foregoing account has reference only to what may be termed aniline colours, the great chapter on the history of technical chemistry, with which Hofmann's name is indissolubly linked.

An entirely new chapter in coal-tar chemistry opens in 1868, when Graebe and Liebermann (in connection with their researches on quinones) made their great discovery of the artificial formation of alizarin from anthracene. They patented their process in Germany

in October, and in this country on December 18th of that year. Their process, it is well known, consisted in producing dibromanthraquinone, either by brominating anthraquinone in sealed tubes, or by oxidising tetrabromanthracene, and subsequently displacing bromine by hydroxyl, by fusion with alkali.

This discovery for the first time of a method of obtaining a vegetable colouring matter artificially was, however, as it stood, of no practical value, as such a process could not be carried out on a large scale.

But why should this be mentioned here? It may seem that any reference to the alizarin industry is out of place in a notice designed to elucidate Hofmann's influence on the development of our knowledge of products derived from coal-tar, as he apparently never took any part in the investigation of anthracene derivatives. Yet it is to his influence that I can trace back my interest in the subject, for, as mentioned early in this account, the very first subject in research which he suggested to me was to prepare a nitro-compound and a base from anthracene. In the course of this work I not only became thoroughly acquainted with this hydrocarbon, but also prepared anthraquinone and other derivatives of it, and consequently was, perhaps, more fully prepared than any other chemist of the day to appreciate the discovery of the relationship of alizarin to anthracene, and was naturally impelled at once to attempt to adapt it to practical requirements. It is more than probable that I should have paid but ordinary attention to Graebe and Liebermann's work had I not possessed an early attachment to anthracene, and I am glad to recognise that I owe this to the knowledge and insight of my great master.

Being aware of the importance of alizarin as a colouring matter, and having some quantity of anthracene and anthraquinone left over from my experiments at the Royal College of Chemistry, I commenced to experiment on the formation of this substance, with the object of finding a process by which bromine might be dispensed with.

I knew of the remarkable stability of anthraquinone: that it could be crystallised from concentrated sulphuric acid without undergoing change, and that in making a combustion of it, if the operation were at all hurried, part of the anthraquinone would pass through the heated tube, and condense at the cool end unaltered.

Moreover, not long before I commenced to work at the artificial formation of alizarin, namely, in 1867, Wurtz and Kekulé had shown that when benzenesulphonic acid was heated with potassium hydrate, it gave phenate and sulphite; and Dusart had also found that naphthalenedisulphonic acid was in like manner converted into a dihydroxynaphthalene; so that it appeared probable that if a disulph-

onic acid of anthraquinone could be obtained, it would be possible to convert it by the new reaction into alizarin.

Anthraquinone was therefore heated with oil of vitriol more and more strongly, until the boiling point was nearly reached, as I was determined either to obtain a sulphonic acid or destroy the anthraquinone; and at last it was found that the anthraquinone had disappeared, yielding a product which was soluble in water. After the excess of sulphuric acid had been removed in the usual way with barium carbonate, the product was fused with caustic alkali, and to my delight it changed first to violet, and then became black from the intensity of its colour. On dissolving the melt, a beautiful purple solution was obtained, which gave a yellow precipitate when acidified, and on examination this was found to dye mordanted cloth like garancine.

On the 20th of May (1869) I sent dyed patterns to my friend Mr. Robert Hogg, of Glasgow, who had a very large experience in reference to madder and garancine, and also of the coal-tar colours from the days of the mauve dye, whose opinion I valued very much in all practical matters connected with dye-stuffs, especially from a commercial point of view, and he was very favourably impressed with the results I had obtained. This process, however, was not patented until June 26. (About the same time as I discovered this process, Graebe, Liebermann, and Caro quite independently arrived at the same result in Germany.) This process has proved the most permanently important one yet discovered, and is the one still universally used. I was also fortunate enough to discover a second process, which was of great value in the early days of the industry, but is not in use now so far as I know. It consisted in the use of dichloranthracene as the starting point, instead of anthraquinone. This substance was found to readily afford a sulphonic acid, which could be easily changed into anthraquinonesulphonic acid, either by oxidising its solution with manganese dioxide or more simply by heating it with sulphuric acid. This process was patented in November, 1869.

After discovering processes by which artificial alizarin could be produced, the technical value of the artificially prepared dye-stuff had to be ascertained. Experiments were soon made by the calico printers, as no new processes had to be discovered for the application of this colouring matter, those in use for madder and garancine being suitable. Turkey-red dyers also experimented with it, but some were not so successful as others, for reasons easily understood afterwards, when the properties of anthrapurpurine, which it contained, were better known.

The subject of price, however, was the important question, because

this product had to compete with those already in the market, namely, madder and garancine, and therefore high prices could not be obtained as in the case of a new dye.

Before this could be settled, the first thing necessary was to get a supply of anthracene. This substance was not at this date separated by the tar distillers, there being no use for it; many of them, in fact, knew nothing of its existence, and the question as to whether it could be obtained in sufficient quantity and at a sufficiently low price had to be settled.

But experiments I had made on the small scale, on the distillation of soft pitch, at the Royal College of Chemistry, gave me confidence, and my brother and I entered into the matter with great energy.* At first we prepared anthracene by distilling pitch ourselves, and thought of using this as a source of this hydrocarbon on an extensive scale, as we felt it was capable of yielding a considerable supply. We knew, however, that it could also be obtained from the last runnings of the tar stills, from which it crystallised on cooling. My brother, therefore, visited nearly all the tar works in the kingdom, and showed the distillers how to separate the anthracene, promising to take all they could make, and in this way a sufficient and rapidly increasing supply for our requirements was soon obtained of all sorts of qualities, some being not much thicker than pea soup, from the imperfect way in which it was drained. Very few tar distillers in those days had hydraulic presses, such as are now used, with which they could free the solid from the excess of oil. The value of the anthracene was estimated by washing with carbon bisulphide, afterwards alcohol was used, but for our own purposes we all along used an anthraquinone test. This method was afterwards worked out more perfectly on the Continent, and made a practical test for both the buyer and seller; but at the time I am writing of tar distillers were not sufficiently educated in such matters to use any but very simple tests.

The purification of the anthracene sufficiently for our purpose had then to be worked out, and in doing this I found out a curious fact, namely, that when distilled with caustic potash it was much improved in quality—considerably more so than when distilled either alone or with caustic soda. And potash distilled anthracene was especially necessary when dichloranthracene had to be prepared, as it yielded a well-crystallised, easily purified product, whereas anthracene which had been distilled, either alone or with caustic soda, gave a badly-crystallised, sticky product, which was very difficult to purify.

On examining into the action of caustic potash on anthracene, it was

* My father, to whose great kindness I was so much indebted, died in 1864, so that our firm then consisted only of my brother and myself.

found that if, after the anthracene had been distilled off, the residue was freed from alkali by washing, and then distilled, a substance very like anthracene was obtained, which Graebe subsequently found to be the nitrogenous compound now known as *carbazol*. It is by means of caustic potash that this substance is now separated from crude anthracene, and the process is still used to a large extent to improve the quality of anthracene. All the anthracene we used at Greenford Green was treated in this manner.

The purification of the anthraquinone was at first effected by sublimation, followed by crystallisation. A good deal of difficulty was experienced in the conversion of this substance into its sulphonic acid, however, and at the high temperature at which combination took place, the formation of steam from the water produced at the same time led to considerable quantities of the anthraquinone becoming sublimed, which, although not lost, yet was a source of trouble in various ways. The means of overcoming this difficulty was to use fuming sulphuric acid, with which anthraquinone combined at a much lower temperature, but the only acid of the kind then made was the old-fashioned Nordhausen acid. We imported a quantity of this, and, of course, found it to work satisfactorily, but the difficulties and expense connected with the carriage and transport of this substance on account of its dangerous nature—supplied as it then was in large earthenware bottles—made it unsuitable for use in this country.

The artificial alizarin we first made was produced by the anthraquinone process, the method still used for its manufacture, but the difficulty in preparing the sulphonic acid in those early days just referred to caused us to turn our attention to the second process I had discovered, in which dichloranthracene was used. After finding out the best way of preparing the substance, our difficulties in reference to the sulphonic acid vanished, as dichloranthracene dissolves easily in hot ordinary oil of vitriol, producing dichloranthracenedisulphonic acid; on continued heating this acid oxidises, hydrogen chloride and sulphur dioxide being evolved and anthraquinonedisulphonic acid formed. Without this process, the manufacture of artificial alizarin in this country could not have been carried on with much success in the early days of its manufacture.

The conversion of the anthraquinonesulphonic acids into colouring matter by treatment with caustic alkali at a high temperature at first presented many difficulties when carried out on the large scale. Our earliest experiments were made by heating the mixture in iron trays in a large air bath. Mixtures of caustic potash and caustic soda were also experimented with instead of caustic soda alone. Then the mixture was placed in a revolving cylinder, heated in an

air bath, small cannon balls being put into the cylinder to mix the product. But all these methods were only partially successful, the percentage of colouring matter produced not being so high as it should have been. At last heating in a very strong iron boiler under pressure was resorted to, and by adopting this method—which is now that universally used—we obtained a satisfactory result.

From the experiments we made in 1869 we felt pretty confident that artificial alizarin could be made at a price to compete with madder and garancine, and before the end of the year we had produced 1 ton of this colouring matter in the form of paste, in 1870 40 tons, and in 1871 220 tons, and so on in increasing quantities year by year.

The colouring matter produced from dichloranthracene was chiefly anthrapurpurin containing a little flavopurpurine. Theoretically it should have consisted of these products only, but owing to the occurrence of a secondary action, which I need not refer to here (see *Lectures Soc. Arts*, May 30th, 1879), it also contained alizarin, which we sometimes separated when required for dyeing purples. This colouring matter yielded a shade of colour which answered most of the requirements of the consumers for some time, as it was chiefly used by the Turkey-red dyers, and the supply being limited, it was often used in combination with garancine, as in this way more brilliant reds could be obtained than when using garancine alone, though, of course, the use of the artificial colouring matter alone yielded still clearer and more fiery shades.

Dichloranthracene was afterwards found to yield a monosulphonic acid when treated with sulphuric acid, provided the temperature were kept low and the amount of acid limited; and when oxidised with manganese peroxide or other oxidising agent, this yielded anthraquinonemonosulphonic acid, from which alizarin alone could be obtained. But the properties of dichloranthracenemonosulphonic acid were such, and the technical difficulties of carrying out the process so considerable, that it was never used very successfully. Moreover, by this time, fuming sulphuric acid had come into use, and anthraquinonemonosulphonic acid could be more readily produced directly from anthraquinone. As we had been successful in producing artificial alizarin, others did not run much risk in following our lead; yet, up to the end of 1870, the Greenford Green Works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country.

From the foregoing, it is seen that, as in the case of the aniline colours, all the pioneering work connected with the foundation and

establishment of this branch of the coal-tar colour industry was also done in this country.

For the due development of this industry, it was necessary not only to attend to technical processes, but also to carry on scientific research in connection with it. Early in 1870, I had the honour of bringing before this Society an account of some experiments on the formation of the colouring matter obtained from the sulphonic acids of anthraquinone, showing that it contained alizarin possessed of both the chemical and optical properties of that obtained from madder root. At the same time, attention was directed to the existence of a second colouring matter, yielding reds more scarlet and purples of a bluer shade than alizarin (*J. Chem. Soc.*, 1870, **23**, 133). This second colouring matter was afterwards made the subject of further investigation, and shown to be an isomer of purpurin; it was therefore called *anthrapurpurin* (*J. Chem. Soc.*, 1872, **25**, 659, and 1873, **26**, 425). Dichlor- and dibrom-anthracene and their disulphonic acids, &c., were also investigated. Anthraflavic acid, discovered by Schunck in some secondary products sent to him from my works, was made the subject of two researches; in the first of these, this compound was shown to be an isomer of alizarin, and not to contain C_{15} , as supposed by its discoverer. In the second, the sublimed acid was examined and found to be identical with the unsublimed; it was also shown that when fused with alkali it did not yield alizarin, as stated by Schunck, but a colouring matter yielding orange-red colours with alumina mordants. This, Schunck and Roemer, some time afterwards showed to be another isomer of purpurin which was named by them flavopurpurin.

In this investigation, anthraflavic acid was found to yield a diacetyl and dibenzoyl derivative, which was evidence that it contained two hydroxyl groups like alizarin (*J. Chem. Soc.*, 1873, **26**, 19). Later on, an investigation was made on the formation of anthrapurpurin, proving that, as in the case of flavopurpurin, the formation of the colouring matter from the disulphonic acid of anthraquinone is preceded by that of a dihydroxy-derivative, also an isomer of alizarin, now known as *isoanthraflavic acid*, which, when heated with caustic alkali, is partially oxidised into anthrapurpurin and partially reduced (*J. Chem. Soc.*, 1876, i, **29**, 851). Besides these, the formation of bromalizarin (*J. Chem. Soc.*, 1874, **27**, 401), of β -nitroalizarin (*J. Chem. Soc.*, 1876, ii, **30**, 578), of anthrapurpuramide (*J. Chem. Soc.*, 1878, **33**, 216), and of the dibromanthraquinones discovered by Graebe and Liebermann and the colouring matters obtainable from them, were investigated (*J. Chem. Soc.*, 1880, **37**, 554). Much work has also been done in reference to this industry by Graebe and Liebermann and other investigators.

The manufacture of artificial alizarin in Germany has been almost

entirely confined to the anthraquinone process, fuming sulphuric acid being used in the preparation of the sulphonic acids. For this purpose very strong acid, containing about 40 per cent. of anhydride, was made from Nordhausen acid, and used until the process of making sulphuric anhydride by decomposing sulphuric acid into sulphurous oxide, oxygen, and water, and recombining the two former, was introduced.

After being engaged in the coal-tar colour industry for 18 years, my connection with it, technically, came to an end in 1874, when the alizarin industry had been well established and was rapidly extending.

On looking back over the period, it is of interest to see the wonderful progress the industry had made up to that time—a progress which was going on by leaps and bounds. I have no statistics connected with the precise period, but four years afterwards, namely in 1878—with the kind assistance of Dr. Caro—an estimate of the value of the colours produced during that year was obtained, at a time when the industry had just passed its majority and was 22 years old. The sum amounted to £3,150,000. (See *Jour. Soc. Arts.*, May 30, 1879.) Of its present position, it is very difficult to speak. Certainly its progress has been very great since 1878; but chiefly owing to the scientific skill bestowed upon the production of the colouring matters, their cost has been greatly diminished, so that I understand rosaniline hydrochloride, which once was worth about £3 3s. per ounce, may now be purchased at 2s. 9d. per lb., and aniline at less than 6d. per lb.

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During the early days of the coal-tar colour industry, the complaint was made that the prosecution of purely scientific chemistry was being injured by its influence, as chemists were everywhere experimenting with aniline and other products, with objects of a more selfish than scientific character. It is probable that there was some truth in this for a time, but it was not long before a welcome change set in, and the work carried on in relation to this industry was soon conducted in a scientific spirit, even when the result sought for was expected to be of technical, as well as where it was expected to be of scientific, value. But the amount of work carried on from the latter point of view increased more and more, as interesting questions connected with the colouring matters and the methods by which they were produced presented themselves to chemists, and now if we look back and consider what has been accomplished, we find that this industry has directly and indirectly had a most marvellous influence on the advancement of

chemical science, especially that part of it relating to the aromatic series of compounds. No other industry in existence can at all be compared with it from this point of view. This has arisen from a variety of circumstances, one of which is that it has not been carried on by the rule of thumb method which has been so common in other cases. Again, as it has utilized the discoveries of chemists, it has handed back to them in return new products which they could not have obtained without its aid, and these have served as materials for still more advanced work: this kind of exchange, indeed, has been going on so repeatedly, that products formerly of the rarest and most complex character are now quite common substances in the coal-tar colour works.

We knew that aniline was at first a rare substance, and when it was afterwards proposed to use ethyl and methyl iodides in the preparation of ordinary dye-stuffs, it seemed incredible that such substances could be introduced for such a purpose as already mentioned, substances which were but rarely met with even in chemical laboratories: but what are these compared with the substances now in use?—their names would be too numerous to mention. One of the most striking facts connected with this industry is the remarkably rapid way in which it has utilized new discoveries which have often been no sooner made than they have been practically applied. This no doubt arises from the fact that an ever increasing army of highly trained and highly gifted chemists are engaged in the industry, especially on the Continent, provided with splendid laboratories, libraries of scientific works and all the most advanced appliances required in scientific research; and the members of this army are not only making discoveries themselves and applying them, but are always on the alert to make the discoveries of others subservient to the industry.

As I have already mentioned, when this industry was first instituted, organic chemistry was comparatively in its infancy, especially if we regard it from our present standpoint. Kekulé had not then brought forward his remarkable benzene theory, and after he had done so its bearings required much elucidation before their importance was well understood. Only solid toluidine was known, orthotoluidine not having been discovered, although it was constantly present in the high boiling aniline used in making rosaniline; but now the facts connected with the ortho-, meta-, and para-position in substances containing the benzene nucleus, or of the α - and β -positions in the naphthalene series, are among the most important to be considered in the manufacture of colouring matters; in fact, this industry has done more to accentuate the importance and character of these positions than any other kind of experimental work.

Although at the commencement of the industry a good deal of work of a purely experimental character had to be done, nevertheless, from the first it was carried out on scientific lines, and this characteristic increased very rapidly, as is seen by the early date at which mauve and magenta were obtained in the pure crystallised condition: it was at this period, as previously stated, that Hofmann commenced his researches on rosaniline and its derivatives, and on other colouring matters, and these researches, taken with those of others, bear out the observations which have just been made. In looking over the work of Hofmann in this field, all who have had experience in the investigation of the subjects he undertook must realise that they presented no ordinary difficulties, especially as for some time he had nothing to guide him in his conclusions but the analytical results. In the early days of organic chemistry, it is well known that on finding colouring matters in the products they were examining, chemists usually regarded them as impurities, and the use of animal charcoal and other means were resorted to for the purpose of getting rid of them; and those who undertook the examination of colouring matters themselves were considered as bold men, and not likely to get much result from their labour. Doubtless, there was much truth in this. Hofmann, however, *was a bold man*, and not one to be daunted, but rather inspired, by difficulties; and from his results we see how great his success was in this department of chemistry, some of his work proving to be of direct practical value, whilst other parts possessed important bearings both on the practical and scientific development of this subject. His researches on colouring matters extended over a quarter of a century, commencing in 1862 with rosaniline, and ending in 1887 with quinoline red; and during that period there were but few years in which he did not produce one or more investigations, either related to colouring matters or the products connected with their production.

It will be obvious from what has been said, how Hofmann's early work—after that of Faraday, Unverdorben, Runge, Fritzsche, Mitscherlich, and Zinin—continued to pave the way for the introduction of the coal-tar colour industry, also how the important influence he exercised on the training of his students led in the same direction. I especially refer to Mansfield, who did such valuable work on coal-tar, and Nicholson, whose chemical education under Hofmann was such an important preparation for the work he undertook in after years on rosaniline and its derivatives; and if I may speak for myself, I can only say how much I owe to Hofmann's training, which fitted me to carry out the work which fell to my lot in connection with the introduction and development of this industry. Then if we further consider the importance of the beautiful researches Hofmann

made, some of which yielded practical results, throwing fresh light on the nature of the colouring matters and products related to them which were obtained as time went on, some idea may be formed of the contributions made by Hofmann and his school to the coal-tar colour industry.

And yet we must bear in mind that his work in this department of chemistry represents but a small part of all that he accomplished—indeed, the amount of scientific work he did was something marvellous.

Notes on Hofmann's Scientific Work.

By HENRY E. ARMSTRONG.

“The eye may rest with complacency upon the simple beauty of the law which governs the construction of the bodies belonging to the type of ammonia.”

The accounts of Hofmann given by Lord Playfair, Sir Frederick Abel and Dr. Perkin are of the greatest value, as affording us the means of knowing the conditions under which he was placed in this country, as well as of understanding the man and the marvellous influence he exercised on all who enjoyed the advantage of working with him. Dr. Perkin's autobiographical reminiscences, and his frequent references to others who laboured successfully in the same field with himself—who, like himself, had been pupils under Hofmann—are a striking testimony to the value of the training imparted by the great master; and this has received even fuller recognition from those who were influenced only at a distance, notably in Dr. Caro's masterly monograph published in 1892 by our German colleagues, as well as in the address delivered by Professor Tiemann shortly after Hofmann's death.

When we take into account the state of knowledge at the present day, and the conditions under which we now work, the contrast which the pictures painted by our three essayists present is indeed a striking one. Starting in times of what may fairly be called rudimentary civilisation, when chemistry could scarcely be called a science, so incomplete and uncoordinated was our knowledge, even ere 50 years are lapsed, we find ourselves in an age of luxurious material profusion, equipped with an extraordinary wealth of new and potent methods of inquiry; methods which have already enabled us to penetrate deeply into the inner mysteries of nature in a manner which must have been altogether inconceivable in Hofmann's early days—for, as Dr. Perkin tells us, those were times when the constitution of compounds was worked out on simple arithmetical lines.

And the progress of the industry which it will ever be the proud

boast of the Hofmann school to have founded is even more marvellous; no fairy tale can match its wonders. Moreover, as its biographers, Perkin and Caro—the two men who, with Hofmann and Nicholson, have done most to develop it—imply, the doctrine that action and reaction are equal and opposite was never more strikingly illustrated, the effect produced by the translation into practice of the results of inquiries undertaken with purely scientific objects in view having almost invariably been followed within a short time by the fullest repayment, in the form either of materials needed by the scientific inquirer or of new problems for investigation, and that apart from the encouragement afforded to workers by the prospect of material rewards. The example thus set has spread to other industries. All who have studied the question are agreed that it is impossible to overrate the share borne by Hofmann, both directly and indirectly, in promoting such progress; to repeat words the present writer used on the occasion of the memorial meeting, we are indebted to him probably to a far greater extent than we shall ever be able to realise, and he will undoubtedly rank among the chemists of the Victorian era as second only to his great master, Liebig—to whom, indeed, he bore the greatest resemblance, in being possessed of most unusual powers of influencing others and of inciting them to work.

Hofmann's own prescience in appraising the national value of science was remarkable, and it is clear that the influence he exercised in introducing scientific method into industry was in no sense accidental, but the considered expression of innate convictions. This is clearly shown by his "Remarks on the Importance of Cultivating Experimental Science in a National Point of View," the substance of a lecture delivered at one of the evening meetings of the College which is appended to the preface to the volume of *Reports of the Royal College of Chemistry and Researches conducted in the Laboratories in the Years 1845-47*, published in 1849. In concluding this he says—

"My principal object, on the present occasion, has been to insist upon the importance of cultivating natural science in its bearings upon the whole mechanism of society, as the mainspring both of individual and national prosperity; and I cannot conclude more appropriately than in the words of the venerable Humboldt, one of the most distinguished philosophers of the present age: 'An equal appreciation of all parts of natural knowledge is an especial requirement of the present epoch, in which the material wealth and the increasing prosperity of nations are in a great measure based on a more enlightened employment of natural products and forces. The most superficial glance at the present condition of European states shows that those which linger in the race cannot hope to escape the partial diminution, and perhaps the final annihilation of their resources. It is with nations as with nature, which, according to a happy expression of Goethe, knows no pause in

increasing movement, development, and production, attaching a curse to standing still.

“Those states which remain behind in general industrial activity, in the selection and preparation of natural substances, in the application of mechanics and chemistry, and in which a due appreciation of such activity fails to pervade all classes, must see their prosperity diminish, and that the more rapidly as neighbouring states are meanwhile advancing, both in science and in the industrial arts, with, as it were, renewed and youthful vigour.’
—*Cosmos*.”

A suggestive paragraph occurs in Lord Playfair’s notice which may well be read in connection with this quotation from Humboldt. It is a grave question whether Hofmann was not led to accept the invitation to quit this country and return to his fatherland because he was able to fathom the hopelessness of the situation here, and foresaw—as events have proved—that Humboldt’s countrymen alone could appreciate his warning. Perhaps he felt our insular conservatism to be beyond even his powers, and understood that men like Perkin and Nicholson had but strayed into industrial pursuits, and were in no sense representatives of the English character. Whatever may be the explanation, it cannot be denied that the higher chemical industries have rapidly retrograded in this country almost from the moment of Hofmann’s departure; and it can scarcely be doubted that had he continued to exert his unrivalled personal influence, our manufacturers would long ere this have been persuaded to follow the methods so successfully adopted by others, and to fully avail themselves of the services of well trained scientific assistants.

Seeing that no scientific man has ever more directly influenced industry, it is interesting to note that, at the very outset of his career, Hofmann entered into direct and intimate relations with industrial workers; in fact, in his first paper he expresses his indebtedness to his friend Ernest Sell, in whose asphalt works at Offenbach, on the Main, the crude basic oil he used in his research was separated from Belgian tar; the association thus established appears to have had a determinative influence on his whole life. This fact is of no slight importance.

In order to understand Hofmann’s services to science, it is necessary to consider his work as a whole, not merely that relating to colours, which after all is to be regarded as but a single episode in a remarkably varied career. It is indeed remarkable how much of what is now the framework of our science is traceable to his labours. In order that this may be realised, it will often be desirable to quote his own clear and graphic statements, sometimes at considerable length; their style is at all times characteristic; and they are of considerable historical interest, as showing how discoveries of such

fundamental importance were arrived at and that devotion to the highest scientific aims is compatible with the existence of the greatest possible interest, and even active participation, in industrial pursuits. Hofmann may be said, indeed, to have been a technical chemist *par excellence*, and his school the type of a true technical school; it is the infusion of the spirit in which he worked into German chemical industry that undoubtedly has led this to achieve such marvellous results, especially during the past five and twenty years.

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His first investigation was published in 1843, in *Liebig's Annalen* (47, 37—87), under the title "Chemische Untersuchung der organischen Basen im Steinkohlentheeröl."* He concludes with the warmest expression of thanks to his teacher—Professor Liebig—in whose laboratory the work had been executed. With remarkably few exceptions, all his subsequent investigations are clearly the logical outcome of this his earliest inquiry. Seldom has an original worker proved so true to his first love, but seldom has a worker fallen on a theme permitting of such infinite extension.

We not only find the key to his later work in this paper. The power of exposition of which he became so great a master is already beginning to show itself, although the highly polished diction and cosmopolitan wealth of expression which so distinguished his later writings are not yet in evidence; these were probably in part derived from his philological training—of which Lord Playfair reminds us—but doubtless also largely the outcome of inherent qualities of mind, reflections of the inner man. But finish of style and completeness are equally apparent in the work itself, and it is obvious that the care which he devoted to the illustration of his lectures, and the insistence on the purification of any substance to be dealt with in an investigation, to which Dr. Perkin refers, were also but expressions of his innate character.

The finished style of his early work, which presumably was entirely his own, appears all the more remarkable when we bear in mind that—as all who were associated with him tell us—he was himself a most awkward manipulator; and that the success he afterwards achieved was due to his extraordinary power of inciting others to work, and to the remarkable judgment he displayed in selecting helpers gifted with powers of experimenting with which himself he was so indifferently endowed. And the manner in which he returned his thanks was equally striking and characteristic; indeed, if the complimentary references in his papers to those who at various times

* The same paper was subsequently published in the *Philosophical Magazine*, 1844, 24, 115, &c., under the title "A Chemical Investigation of the Organic Bases contained in Coal-gas Naphtha."

assisted him were collected, they alone would afford an interesting and matchless record of his diplomatic talents and courtly manners.

His work on coal tar was published less than ten years after Runge (1834) had discovered in that substance *kyanol*, *leukol*, *pyrrol* and *carbolic acid*, no one of which he analysed, however; but Laurent, shortly before Hofmann's work was carried out, had ascertained the composition of carbolic acid and had termed it phenyl hydrate. Judging from his own statement, Hofmann appears to have been led to undertake the investigation of Runge's *kyanol* and *leukol* because they were described as basic substances, at a time when such substances were attracting special attention in Liebig's laboratory, and he only refers to Fritzsche's *anilin*, Unverdorben's *krystallin* and Zinin's *benzidam* after describing his work on *kyanol*. According to Professor Tiemann, however, Liebig had proposed to him to clear up the relationship of *anilin*, *benzidam* and *krystallin*, which Erdmann had suggested were identical, and Professor Tiemann leads us to suppose that the examination of Runge's *leukol* was incidental to this inquiry, but of this there is no mention in the paper. -

Hofmann separated *kyanol* from *leukol*—he obtained only about 1 per cent. of basic oil from the heavy tar oil—by distillation, but purified it by conversion into the oxalate, which he recrystallised from absolute alcohol. He fully described its properties, several of its salts, and its more characteristic actions. At the close of the paper, he describes a number of important observations on its behaviour with a mixture of muriatic acid and potassium chlorate—an agent already applied by Fritzsche to *anilin*—obtaining chloranil, which Erdmann had previously prepared from isatin and chlorine; *benzidam* was shown to behave similarly. By the action of chlorine, he obtained products identical with substances previously prepared by Erdmann from indigo, one of which he recognised as trichlorinated phenol, Laurent's chlorophenissic acid. Nitric acid, in like manner, was found to produce picric acid. Important use was made of these observations: the simultaneous production of phenol and *kyanol* on distilling coal, and the formation of the same chlorinated and nitrated compounds from both, leading him, in fact, to regard them as related compounds, and accepting Laurent's view that carbolic acid was the hydrate of the oxide of an organic radicle, $C_{12}H_{10}$, *phen*, he represented *kyanol* as the amide of the same radicle—as *phenamide*, $C_{12}H_{10} + N_2H_4$. Futile attempts to convert phenol into *kyanol*, made from this point of view, are then referred to.*

* A short time afterwards, however, Laurent and Hofmann succeeded in effecting the conversion. The note on the subject which Laurent communicated to the French Academy on December 26, 1843 (*Compt. rend.*, 17, 1366) has apparently not received the attention it deserves; no better evidence could be given of the

The clearness of Hofmann's theoretical conceptions at this time does not appear to have been sufficiently recognised; yet it is certain that he did far more than merely discover aniline in coal tar and prove its identity with certain products from other sources: he at once saw that he had discovered not a substance only, but a problem. Moreover, after objecting to the name *kyanol*, because it was made up of words from two languages, one of which was already appropriated; and also to *anilin* and *benzidam* as defining its relation to certain classes of compounds, and therefore undesirable, as it could

extent to which he was in advance of his time, even as regards the constitution of bases like aniline. Laurent writes as follows:—

Sur un nouveau mode de formation de l'aniline. M. AUG. LAURENT.—J'ai entrepris avec M. Hofmann quelques recherches ayant pour but de préparer l'aniline. Je pense que les idées qui nous ont servi de guide dans ce travail pourront intéresser les chimistes.

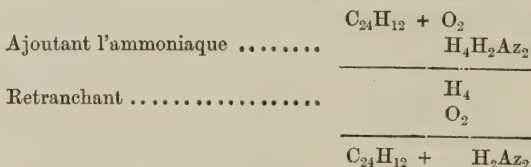
L'aniline pouvant être considérée comme l'amide de l'acide phénique,



Nous pouvions espérer de transformer l'acide en amide, en faisant réagir l'ammoniaque sur lui. On devait avoir :



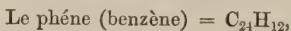
Comme le phénate d'ammonium se décompose très-facilement par la distillation en acide et en ammoniaque, nous avons d'abord essayé de faire réagir ces deux corps à une température rouge, mais sans avoir l'espoir de réussir. En voici la raison, telle que je l'ai donné à M. Liebig, qui assistait à notre expérience. Supposons que l'ammoniaque puisse réduire, à une température rouge, l'acide phénique et former de l'eau, on devra obtenir, si les idées que j'ai développées sur la substitution sont vraies, non de l'aniline, mais un composé isomère. En effet, la formule rationnelle de l'acide phénique doit se représenter par



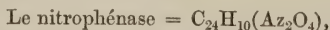
c'est-à-dire, de l'acide phénique dont les deux atomes d'oxygène sont remplacés par deux atomes d'imide.

Or, l'aniline ne renferme pas d'imide, mais de l'amide, ce qui se démontre très-facilement par les deux méthodes qui servent à la préparer.

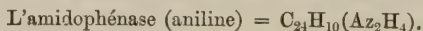
Première Méthode.



il donne avec l'acide nitrique,



celui-ci donne avec l'hydrogène sulfuré, en remplaçant O_4 par H_4 ,



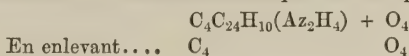
be obtained from so many sources: he suggested the selection of *krySTALLIN* from among the names proposed, *until it should be possible to establish by experiment the scientific name phenamide*. Why he so soon afterwards adopted the name aniline is not evident: no other appears in any of his subsequent papers, except phenylamine when the theoretical relations are under discussion.

Even with the evidence afforded by his first paper alone before us, it cannot be said that Hofmann was not a theorist; it is true that he took little part in the later developments of chemical theory, but it is equally clear on studying his early work that from the very beginning, after he had grasped the fact that phenol and aniline bore a close genetic relation to each other, the whole of his work was based on, and consistently guided by, clear theoretical conceptions. We must remember that during many years he devoted himself to the study of compounds of a very simple type—the amines—and being moulded on such a model, his style naturally became a simple one.

* * * * *

Deuxième Méthode.

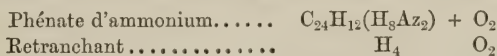
La formule rationnelle de l'acide anthranilique doit se représenter par



On obtient encore l'aniline $C_{24}H_{10}(Az_2H_4)$

J'ajoutai à M. Liebig que nous n'aurions pas réussi que si le phénate d'ammonium eût pu résister à une plus haute température.

En effet, si le phénate d'ammonium ne pouvait se décomposer qu'à 300 degrés, par exemple, cette température serait peut-être suffisante pour permettre à l'hydrogène de l'ammonium de se combiner avec l'oxygène. On aurait alors



Il reste de l'aniline $C_{24}H_{10}(H_4Az_2)$

Notre expérience ne nous donna aucune résultat. L'aniline et l'ammoniaque passèrent dans un tube chauffé au rouge sans se décomposer mutuellement.

Nous avons alors renfermé du phénate d'ammonium dans un tube de verre très-épais que nous avons fermé à la lampe, et nous l'avons exposé pendant quelques instants, dans un bain d'huile, à la température de 260 degrés environ. Après le refroidissement nous avons trouvé des traces d'aniline dans le produit.

Nous avons recommencé l'expérience, mais nous avons placé le tube dans un four dont la température pouvait varier de 100 à 300 degrés, et nous l'y avons laissé pendant deux à trois semaines. En brisant le tube, nous y avons trouvé une assez grande quantité d'aniline. Il est bien évident que la réaction est due à la décomposition du phénate d'ammonium, et non à la décomposition mutuelle de l'acide phénique et de l'ammoniaque, puisque ces deux corps ne réagissent pas l'un sur l'autre à une température rouge.

On entrevoit la possibilité de faire de la quinine, de la morphine, &c., si l'on parvient à découvrir des composés correspondant à l'acide phénique.

The investigation published in 1845, under the title "On the Metamorphoses of Indigo. Production of Organic Bases which contain Chlorine and Bromine" (*Chem. Soc. Memoirs*, February, 1845, **2**, 266), must be regarded as the real starting point in Hofmann's scientific career. To this is appended the following memorable postscript—

"I have had the pleasure of witnessing the care and accuracy with which the author of this paper has proceeded in making his observations and establishing his facts. It appears to me that he has produced a definite and irrefragable proof that the chemical character of a compound does not depend, as the electro-chemical theory supposes, upon the *nature* of the elements it contains, but solely on the manner of their grouping."—JUSTUS LIEBIG.

Admirable in conception, execution and clearness of statement, this memoir is full of interest, owing to its importance in the history of our science. The work was brought forward at a time when the contest was at its height between the substitution theory and the electro-chemical dualistic theory of Berzelius—the theory that every compound is formed of two constituents, one electro-positive the other electro-negative. Only eight years before, Laurent—we read—had laid down the following law—

"In many organic compounds, by the action of chlorine, a certain number of equivalents of hydrogen are eliminated in the form of hydrochloric acid; the eliminated hydrogen being replaced by a like number of equivalents of chlorine, in such a manner that the chemical character and the fundamental properties of the original compound are not sensibly altered. The chlorine molecules, therefore, must take the place of the hydrogen molecules, and play in the new compound the same part which was performed by the hydrogen molecules in the original."

Although these views met with great opposition at first, many facts were subsequently discovered by Dumas and others which gave the strongest support to Laurent's views, but when Hofmann began his work *No organic base*, he tells us, *was known in which the hydrogen had been replaced by chlorine* in such a manner as not to materially change its properties. And yet, he adds, it would be an argument of the greatest weight, were chlorine, an electro-negative element, to be introduced into a compound possessing electro-positive properties without, however, changing its chemical character. Hence, he undertook his research, and naturally resorted to aniline.

He had already chlorinated aniline, and had obtained, along with much trichlorophenol, a very small quantity of a neutral substance which he only subsequently recognised as trichloraniline; and Fritzsche had prepared tribromaniline, with which he was well acquainted. But Hofmann was in no way misled by these observations—he recognises that—"In these cases the action has evidently gone too far for the aniline still to preserve its original character, and

it remained therefore to try in some way to regulate the action so as to produce compounds in which only one equivalent of hydrogen was replaced, and which, like aniline, might possibly possess basic properties." He therefore repeated his earlier experiments, and attempted to chlorinate aniline, but failed to obtain better results.

Failure to Hofmann, however, even at this early date as ever afterwards, was but the incentive to renewed efforts. At once it occurs to him to chlorinate anthranilic acid, in the expectation that—as this acid was known to yield aniline on distillation—the chlorinated acid would afford the desired chloraniline; and he further foresees the probability that nitrobenzene would yield a chlorinated derivative which would require only to be treated with sulphuretted hydrogen to be changed into the desired compound. But while engaged in preparing anthranilic acid, "another expedient offered itself," he tells us, "which by changing completely the direction of my researches led me quickly to the desired object." Remembering that it was not necessary to convert indigo into anthranilic acid in order to obtain aniline, but that this latter might be directly produced from it "*as a true product of oxidation*" by distillation with potash, he asks is it not in the highest degree probable, not to say certain, that isatin, a product of the oxidation of indigo, will be converted into indigo by fusion with potash; in which case the chlor- and dichlor-isatin already described by Erdmann may be expected to give chlor- and dichlor-aniline.* The experiment with isatin proving successful, mono- and dichlor-aniline were easily prepared.

It is impossible not to recognise that the train of argument thus made use of, at a time when so little was known of constitution as we now understand it, was eminently philosophical and comprehensive, and this is equally true of his treatment of his results. After fully describing a series of chlorinated and brominated anilines, he remarks that no two constructions can be placed on the facts he has discovered. They prove, in an undoubted manner, that in certain circumstances chlorine and bromine can perform the part of hydrogen in organic compounds. But he subsequently adds—

"It appears, however, that the chlorine preserves, to a certain extent, its electro-negative character, in those compounds in which it replaces hydrogen,

* It is clear that Hofmann's attention had at this time been very specially directed to previous researches on indigo, as a very lengthy abstract of the work of Dumas, Erdmann and Laurent, prepared by him, is published in *Liebig's Annalen* at the end of 1843 under the title "Uebersicht der in letzter Zeit unternommenen Forschungen über den Indigo und seine Metamorphosen." This abstract is wrongly included in the Royal Society's Catalogue of Scientific Papers among Hofmann's original contributions.

and that in proportion to the increase in the number of equivalents of the latter, for which chlorine or bromine are substituted, so is this character the more impressed on the resulting compounds. The compound atom aniline, $C_{12}H_7N$, in consequence of the peculiar arrangement of its elements, possesses the property of uniting with an acid; replace one equivalent of its hydrogen by bromine and we obtain bromaniline, a body possessing likewise basic properties, but in a feebler degree, substitute now another equivalent of bromine for hydrogen, and we have dibromaniline. The facility with which all its salts are decomposed evidently indicates that the basic character of aniline is further enfeebled by the repeated assumption of bromine. Finally, in tribromaniline the electro-negative properties of the assumed bromine equivalents have placed themselves in equilibrium with the electro-positive character of the original system."

While confirming the truth of the principle put forward by Laurent, Hofmann therefore clearly recognised the limitations to which it must be subjected; and nothing has since been discovered which would lead us to state the substitution theory in terms other than those he adopted.

It is remarkable to what an extent Hofmann's activity now became manifest, and how rapidly he extended the field of his investigations. At Liebig's suggestion, Dr. Blyth and he undertook the investigation of fluid storax balsam (*Chem. Soc. Memoirs*, **2**, 334, April, 1845). At the same time, recognising the importance of bases, he set to work with Muspratt to apply Zinin's method of reducing nitro-compounds generally; and commencing with nitro-toluene, they discover paratoluidine (*ibid.*, **2**, 367, April, 1845). At the close of the paper, they refer to the production of nitraniline from dinitrobenzene. The subsequent special memoir on this latter subject (*ibid.*, **3**, 111, March, 1846) opens with an elaborate discussion of the action of nitric acid on organic substances and of the nature of nitro-compounds; as we read this we realise how absolutely vague were the ideas which then existed on this subject. But Hofmann's perceptive power is again at once apparent, for the style is so essentially his that there can be no question that his views especially are being put forward. Laurent's diagnosis of the nitro-compounds is singled out as clearly in advance of all others, and the conclusion advocated that

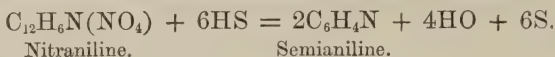
"Many products which have assumed nitrogen and oxygen from nitric acid may indeed be regarded as simple products of substitution, in which the hydrogen instead of being replaced by chlorine or bromine, is replaced by a compound radicle, namely, by hyponitric acid (NO_4)."

As the displacement of hydrogen by hyponitric acid had been limited to acid and neutral substances, it appeared to be a point of great interest to ascertain whether, indeed, NO_4 could also displace hydrogen in basic compounds without destroying their electro-positive character.

Taking into account the various ways in which aniline was formed, its characteristic properties, and, above all, the fact that hydrogen could be displaced in it by bromine and chlorine, they deemed this substance the best suited to their experiments. Failing, however, in their attempt to nitrate it, and also to nitrate isatin, and foreseeing, also, that nitrosalicylamide—a substance prepared by Cahours a short time previously—could not be expected to yield nitraniline, as salicylamide gave but very little aniline on distillation, they asked themselves whether it might not be possible to partially reduce dinitrobenzene. In times when so little was established about the nature of nitro-compounds, such an argument cannot have been so self-evident as it now appears to be, even to the beginner; indeed the fixity of purpose—based, doubtless, on their clear theoretical conception of the nature of the problem they had in hand—displayed by Hofmann and Muspratt on this occasion, is specially noteworthy. Just as they were about to make the experiment, Zinin published a paper in which it was stated that dinitronaphthalene and dinitrobenzene were entirely deprived of their oxygen on reduction by sulphuretted hydrogen; and that, whereas it was to be expected that the former would yield a base corresponding to it in composition, $C_{20}H_{10}N_2$, to judge from the analysis of the platinichloride prepared from the base, its equivalent was only half as great, viz., $C_{10}H_5N$; Zinin, therefore, came to the conclusion that a division had taken place, and, consequently, gave the name seminaphthalidine to the product of reduction. This, it will be remembered, was in days before the importance of Avogadro's law had been impressed on chemists by Canizzaro, when the methods of rigidly determining molecular weights such as we now regularly use were in their first infancy. Zinin's researches—Hofmann and Muspratt tell us—appeared to cut off all hopes of their ever obtaining nitraniline; nevertheless they considered a continuation of their experiments in every way desirable, and soon obtained results which had escaped the observation of Zinin; these brought them to the point they aimed at. As every student of the elements of organic chemistry now knows, nothing is easier—following Hofmann and Muspratt—than to obtain nitraniline from dinitrobenzene; and, moreover, the method of partially reducing nitro-compounds thus introduced by them has proved of service in many other cases. Nitraniline was found to have the properties of an exceedingly weak base. Its production is spoken of as “interesting in reference to the question of substitution, which is still in debate among chemists. If we reject that theory—they remark—we can scarcely understand the constitution of this base and its relation to aniline.”

But, as showing how limited was the knowledge of that time, it is noteworthy that the memoir concludes with a reference to the

compound obtained by Zinin from dinitrobenzene, in which it is pointed out that probably this is but a product of the further reduction of nitraniline in accordance with the equation



Nitraniline.

Semianiline.

Historical facts such as this serve to remind us how great has been the influence exercised by the systematic adoption of physical conceptions by chemists.

Although it was some time before the arguments of Berzelius and his school came to be regarded as futile, the results obtained by Hofmann in the course of his investigations of the chlor- and brom-anilines and of nitraniline had—it is well known—considerable influence on the minds of chemists, and largely promoted the ultimate acceptance of the substitution theory.

* * * * *

A new chapter in Hofmann's work now begins to open; the first reference to this is at the close of his memoir on the metamorphoses of indigo, where we read—

“Before concluding this memoir, I shall mention another compound which appears worthy of the attention of chemists. It is formed by passing into aniline, free from water, a stream of cyanic acid. . . . It is a kind of urea in which the ammonia is displaced by aniline. I was in hopes that this body would possess basic properties, and, like urea, form crystalline salts with nitric and oxalic acid; its properties are, however, very different.”

The theme is still further developed in a brief note on “New Researches on Aniline,” communicated to the Chemical Society in December 1845 (*Memoirs*, 3, 26), the opening paragraph of which is as follows—

“In my former papers upon aniline, I had repeated opportunities of pointing out the remarkable analogy which exists between this body and ammonia, and at the conclusion of my memoirs on chloraniline and bromaniline, I announced the existence of a compound which may be considered as urea in which ammonia is replaced by aniline. The discovery of this substance opened a new field for research, inasmuch as it was to be expected that all the relations exhibited by ammonia, and the metamorphoses it undergoes, might be realised with aniline.”

This theme may be said to have occupied him during the rest of his scientific career, for the elaboration of the chemistry of the amine type soon became the work of his life.

The note last referred to admirably illustrates Hofmann's style, especially his remarkable quickness in perceiving and availing himself of opportunities, his powers of generalisation, and the manner in which, without the slightest loss of time, he proceeded to develop his attack in a variety of directions as soon as a new observation

was made and a new problem indicated. In a few lines we are told that the comportment of aniline with cyanic acid induced him to subject it also to the action of cyanogen and chloride of cyanogen; that sulphide of carbon readily acts on it, forming sulphocarbonilide that, inasmuch as the new substance from urea and cyanic acid might be considered as aniline which had lost one equivalent of hydrogen and assumed the elements of carbonic oxide—as *carbanilide*—it was probable that it might be produced by means of phosgenic gas, and the experiment being tried, such proved to be the case. Finally, reference is made to the action of oil of mustard, of trichloride of phosphorus, and of chloride of silicon on aniline as giving rise to crystalline products.

All these observations were subsequently elaborated, but it was not until several years later that most of them came to fruition. Some considerable time was spent in studying the action of cyanogen and of iodine from the point of view of the substitution theory, as the imperfect knowledge then at the disposal of chemists of the influence of these electro-negative radicles on organic substances seemed to indicate a marked difference between their action and the effects which chlorine and bromine, so analogous in every other respect, produced under the same circumstances.

Hofmann found (*J. Chem. Soc.*, May, 1848, 1, 269) that iodo-aniline may be obtained by the direct interaction of iodine and aniline, and that it was a weakly basic substance. He failed, however, to obtain any higher iodo-derivative, and pointed to the action of the three halogens on aniline as affording an interesting illustration of the decreasing affinity which chlorine, bromine and iodine manifest for hydrogen. It is of interest, historically, that reference is made in this paper to the ingenious process devised by M. Melsens for substituting hydrogen in the place of chlorine in acetic acid by means of a weak amalgam of potassium. Experiments on the process made with Dr. Kolbe when he was in London, are referred to, showing that chlor- and brom-aniline were reconverted into aniline with the greatest facility by its means. We are thus reminded that sodium amalgam was not yet recognised at this time as an all-powerful reducing agent.

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The action of cyanogen on aniline was described before that of iodine (*ibid.*, April, 1848, 159). The product, which, perhaps unfortunately, was named *cyaniline*, proved to be composed of the elements of aniline plus those of cyanogen, not a substitution compound analogous to those obtained by the action of halogens. Toluidine and also cumidine—the base which Nicholson, one of Hofmann's pupils, had described but a short time previously—gave similar pro-

ducts; not only ammonia, but also nicotine and leuconine (quinoline), however, were found to behave altogether differently, and Hofmann takes the opportunity of pointing out that, although they resemble aniline in a great many respects, these two bases seem to belong to a perfectly different class of alkaloids.

Cyaniline is spoken of as the first instance in which an organic alkali is found associated with another compound the presence of which does not affect its saturating capacity—it is regarded as a *conjugated base*, the counterpart of *conjugated acids*, such as formobenzoic and hippuric acids, a view which is practically identical with that now held.

Hofmann, in this memoir, gives utterance to important views on the constitution of the alkaloids generally, whilst guarding himself from entering upon the often disputed question whether they were compounds of ammonia or amidogen—a question which was soon to receive its solution at his hands. The notions of a relation between the amount of nitrogen in organic bases and their saturating capacity, emanating from Liebig's earlier experiments on this subject, lost their significance—we are told—on the discovery of alkaloids containing more than one equivalent of nitrogen Nevertheless, a relation between the nitrogen and the saturating capacity remained extremely probable, and chemists commenced to assume the nitrogen as existing in these bases in two forms. In almost all cases that portion of this element to which the basic properties were referred was believed to be in the form of amidogen, ammonia, or oxide of ammonium, whilst the views respecting the other portion were for the most part less decided. Hofmann then criticises views put forward by Fresenius, based on the composition of nitraniline, pointing out their arbitrary character, and that in a class of compounds so rich as that of the organic bases, a greater variety is to be expected than is admissible on the assumption that they resemble nitraniline. He is willing to admit that possibly some may contain an oxide of nitrogen, and that others may be cyanogen compounds, but adds, however, that a great many other modes of constitution may be imagined which present a similar degree of probability.

Failing to obtain a cyanogen substitution derivative of aniline by means of cyanogen, nothing was more natural than to attempt its preparation by means of chloride, bromide and iodide of cyanogen, and, consequently, we find the third paper of the series entitled "Researches on the Volatile Organic Bases" devoted to this subject (*J. Chem. Soc.*, June, 1848, 1, 285); as indicating the gradual development of Hofmann's views on the constitution of the amines, this paper is full of interest.

It contains an account of *melaniline* (now known as diphenyl-

guanidine), a compound formed by the action of cyanogen chloride and bromide on aniline "produced by the fusion of two aniline atoms which have lost one equivalent of hydrogen in the form of hydrochloric acid, and have simultaneously assimilated a proportional amount of cyanogen." The name appears to have been chosen to indicate the supposed analogy of the substance with the melamine discovered by Liebig. Besides a description of melaniline and its salts, and of dichloro-, dibromo-, diiodo- and dinitro-melaniline, the memoir contains an account of the behaviour of melaniline with cyanogen, which is characterised as remarkable owing to the assimilation of two equivalents of cyanogen, both the aniline atoms (the intimate combination of which constitutes melaniline) exhibiting, it would seem, the same comportment with cyanogen as when in the isolated state.

Hofmann speaks of melaniline as a conjugated base of a similar, although more complicated, constitution than cyaniline. He points out that the capacity which we observe in aniline of combining with other substances without losing its basic properties, has by no means reached its limits in melaniline; in dicyanomelaniline we see two new equivalents of cyanogen enter into the compound, and some preliminary experiments appeared to indicate that this accumulation round the original atom may be carried still farther. "Facts like these," he adds, "deserve particular attention, containing as they do new confirmations of a general view of the organic bases which is daily gaining ground." At a very early period, he goes on to state, as far back as 1837, Berzelius, on the ground of Liebig's researches, expressed the opinion that the natural alkaloids, which at that period engrossed the undivided attention of chemists, were peculiar ammonia compounds—conjugated compounds, in which the chemical character of ammonia, modified, indeed, by its conjunct, was still perceptible. This view, which was principally founded on the remarkable analogy of the ammonia salts with the salts of the alkaloids, met by no means with general approbation when first stated; but it had been retained and carried out by Berzelius with the perseverance and ratiocination which are peculiar to that great chemist, and it could not be denied that since that period science had acquired a great number of facts which powerfully supported his opinion.

He then proceeds, in his clear manner, to dilate at length on these facts, and to interpret them in support of the view held by Berzelius. Finally, we come to the following remarkable passages:—

"All these considerations render it exceedingly probable that the organic bases are indeed conjugated ammonia compounds. It is true we are not able, at present, to isolate the ammonia without entirely destroying the compounds; and it is a question whether we shall ever find a method of

separating and reuniting the proximate constituents which the theory of Berzelius supposes in these alkaloids, in the same manner as we effect the separation and reunion of acid and base in a salt. Vainly have I hoped in the course of my investigations of this subject to see aniline split up into ammonia and the conjunct



"Possibly this separation may succeed in the hands of a more happy experimenter ; possibly it may ever remain unaccomplished ; nevertheless, the adoption of Berzelius's theory will prove a great benefit, even if it were only to aid the memory and to facilitate the study.

"All our formulæ, our whole nomenclature, would be simplified by such an adoption. No longer should we have anilides, naphthalides, and cumidides ; these substances becoming anilo-amides, naphthalido-amides, and cumido-amides ; and by introducing conventional symbols for the conjuncts, every compound might be expressed rapidly and concisely.

"By considering the alkaloids as conjugated compounds of ammonia, cyaniline, and melaniline become conjugated ammonia compounds of the second order, or, in other words, the original ammonia atom has become associated with the conjunct, $C_{12}H_4 = An$, and with other substances, and the rational formulæ of these compounds now assume the following shape—

Ammonia	NH_3 .
Aniline	$NH_3(An)$.
Cyaniline	$NH_3(AnCy)$.
Melaniline	$NH_3(An_2AdCy)$.
Dicyanomelaniline.....	$NH_3(2AnCy, AdCy)$.

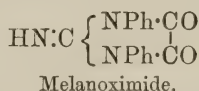
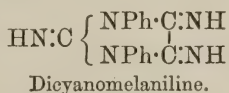
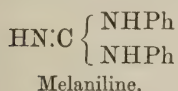
Such fervid advocacy of the Berzelian hypothesis is very remarkable when we recollect that his first experiments with aniline led him to conclude that it was *phenamide*, $C_{12}H_{10} \cdot N_2H_4$; and also that he was the pupil of Liebig, who held a view very different from that of Berzelius, in entire harmony with Hofmann's own early conception of the nature of the base. His attitude at this time towards the great question of the nature of the organic bases is truly striking testimony of the influence then exercised by the great Swede, especially as a few months later the force of facts caused him to return to his original faith ; indeed, to place the truth of Liebig's view beyond all question.

The fourth of the researches on the volatile organic bases deals with the preparation and properties of anilourea (phenylcarbamide) from aniline and cyanic acid, of carbanilide (diphenylurea), and of sulphocarbanilide. It is an unusually tersely written, purely practical communication.

The next (*J. Chem. Soc.*, November, 1849, 2, 300) is of special interest, and marks an entire change of front in Hofmann's views regarding the organic bases. It is divided into several sections, the first of which on the action of acids and bases on cyaniline needs no comment ; the second, on metamorphoses of dicyanomelaniline

records, among other things, the discovery of carbanil (phenyl isocyanate), now an analytical agent of great value in determining the presence of alcoholic hydroxyl.

The gradual evolution of ideas noticeable in this memoir is very striking. The product obtained on subjecting dicyanomelaniline to the action of concentrated hydrochloric acid is a yellowish, indistinctly crystalline substance, $C_{30}H_{11}N_3O_4$. Having in mind the fact that cyaniline was converted under similar circumstances into oxalates of aniline and ammonia, or rather into compounds derived from those salts by elimination of water, Hofmann's insight at once led him to regard the yellow substance as melaniline binoxalate less four equivalents of water, and he shows that it yields melaniline and oxalic acid when subjected to the action of alkali. He then points out that it belongs to a daily increasing class of compounds derived from acid salts of ammonia, or of organic bases, by elimination of four equivalents of water, such as succinimide, and he therefore terms it *melanoximide*, a name which is not inappropriate even from our modern point of view.



He attempts to prepare melanoximide from binoxalate of melaniline, but fails owing to the facility with which melaniline itself decomposes when heated. In carrying out these experiments, however, a "peculiar, somewhat cyanic odour," which had frequently been noticed during the investigation, was developed to an unusual extent, and "I began to hope," says Hofmann, "that I should at last succeed in securing this enigmatical body which I had vainly chased on so many occasions." But he did not succeed until he began to study the action of heat on melanoximide itself. On subjecting this compound to dry distillation, much gas—chiefly carbonic oxide—was disengaged, a yellowish liquid distilling over "of a most powerful odour, recalling at once the odour of aniline, of cyanogen, and hydrocyanic acid, provoking lachrymation in a most fearful manner, and exciting, too, in the throat the suffocating sensation produced by the latter." The quantity of crude liquid obtained amounted to about 10 per cent. of the melanoximide used, and this only when water was carefully excluded, which readily decomposed the liquid. The formula of the new substance is ascertained to be $C_{14}H_5NO_2$, and subtracting from this the elementary difference distinguishing aniline from ammonia, $C_{12}H_4$, the formula of hydrated cyanic acid, C_2HNO_2 is arrived at; the name *anilocyanic acid* is therefore assigned to it. Subsequently he pointed out that as it may also be regarded

as bicarbonate of aniline minus four equivalents of water, the name anilo-carbimid, or in Gerhardt and Laurent's nomenclature the term *carbanite* might be used for the new product.

The chemistry of this remarkable substance is forthwith fully developed, its behaviour being shown to be in all respects similar to that of cyanic acid towards acids, bases and alcohols, attention being specially directed to the formation from it of compounds corresponding to the urethanes previously obtained by Liebig and Wöhler from cyanic acid and alcohols.

Hofmann here gives utterance to the pathetic lament that

"Unable to indulge in a more detailed study of these beautiful reactions in consequence of want of material, I must postpone their completion until a simpler method may have been discovered of obtaining in a shorter time a larger quantity of anilocyanic acid."

He then speaks of the long and complicated series of metamorphoses involved in the preparation of the substance, commencing with that of aniline from indigo or benzole, having caused no small expenditure of time and labour, and recognising how much he was indebted to others, he adds

"Nor could I have found sufficient leisure to follow out the manifold ramifications of the aniline family in its numerous and so often intricately related derivatives . . . had it not been for the valuable assistance and co-operation of Messrs. Nicholson and Abel, assistants in the College of Chemistry."

After further discussing the action of heat on melaniline and melanoximide, Hofmann draws attention to the recent experiments of Wurtz on the compounds of the alcohol radicles with cyanic acid (the cyanic ethers), pointing out that in these substances, as in anilocyanic acid, the original habits of cyanic acid in its behaviour with other bodies are retained in almost every direction, and he therefore groups anilocyanic acid along with them as cyanate of phenyl.* He finds, however, on pursuing the analogy to a practical end that cyanate of phenyl is not produced under circumstances which give rise to the formation of cyanate of methyl—by distilling a mixture of a sulphophenate with cyanate of potash, for example. He also fails in obtaining cyanide of phenyl by distilling cyanide of potassium with a sulphophenate, and is in consequence led to remark on the different behaviour of phenyl alcohol and ordinary alcohols.

Throughout this investigation, Hofmann's attention had been specially directed to the effects produced by the withdrawal of water from the salts of organic bases; and this subject naturally next claims his attention. He arranges the various derivatives of aniline

* It is here apparently that the term *phenylamine* is first used.

formed by the withdrawal of water from aniline salts in a table in comparison with the corresponding ammonia derivatives, and calls attention to the entire absence of anilnitriles or compounds derived from a neutral aniline salt by the elimination of four equivalents of water in the same way that cyanogen is formed from oxalate of ammonia. Experiments are then described which he had made with the object of filling up the blank, but without success. At once the question follows—

“What then, may we ask, is the reason why aniline, which so faithfully imitates the habits of ammonia, refuses to follow its example with respect to the formation of the nitriles? The answer to this question involves a careful consideration of the constitution of aniline and of the analogous bases.”

Reference is then made to the paper before dealt with in which a synopsis is given of the facts supporting the view of Berzelius that the organic bases are conjugated ammonia compounds, in which ammonia pre-exists. According to this view, oxalate of aniline is represented by the formula $\text{H}_3\text{N} \cdot (\text{C}_{12}\text{H}_5)\text{HC}_2\text{O}_4$. But this formula gives no satisfactory answer to the above question. There is no comprehensible reason, Hofmann points out, why the oxalate of ammonia in the aniline salt should not be deprived of its four equivalents of water, and why the residuary cyanogen should not be associated with the usual adjunct.

According to Liebig, however, the organic bases have to be considered as amidogen compounds, and on regarding aniline as an amidogen compound the question appears in a perfectly different light. It is easy to see that the elimination of four equivalents of water from the neutral salt, $(\text{C}_{12}\text{H}_5)_2\text{N} \cdot \text{HC}_2\text{O}_4$, is altogether impossible without the destruction of the term C_{12}H_5 (phenyl). Then comes the following modest reference to the great discovery which must ever rank highest among Hofmann's achievements, as it once for all settled the question that had so long been under discussion, and which was of such immense consequence to the chemistry of the amines and therefore of nitrogen.

“It is probable that considerations like those developed in the preceding pages will naturally assist in the elaboration of more rational views respecting the constitution of the organic bases. The apparent impossibility of obtaining anilocyanogen throws some doubt on the pre-existence of ammonia in aniline. It is probably more in conformity with truth to consider aniline as a substitution product, as ammonia in which part of the hydrogen is replaced by phenyl (he does not appear to remember that he himself took this view originally); and this opinion may, perhaps, meet with the approbation of the Society, if I mention that a series of researches on the action of the bromides of the alcohol radicles on aniline and on ammonia have enabled me actually to replace

the basic hydrogen of these substances, equivalent for equivalent, by the alcohol radicles, and to produce in this manner a numerous series of new alkaloïds which appear to admit of no other mode of interpretation."

* * * * *

We have now to pass to the consideration of Hofmann's "Researches regarding the Molecular Constitution of the Volatile Organic Bases," the first of which was read to the Royal Society on January 17, 1850, having been received on December 26, 1849; it was printed in the *Phil. Trans.*, 1850, 1, 93 (*J. Chem. Soc.*, 3, 279), and was his first communication to the Society.

At the outset, he refers to the two theories of chief importance which had been enunciated respecting the constitution of the organic bases—those of Berzelius and Liebig; after remarking that the former had, in course of time, become more and more generally accepted—by himself among others, as we have seen—he draws attention to his own recent discussion of the question, and to his having shown that the analogy which had been so generally recognised as obtaining between the salts of ammonia and of the organic bases broke down just at the point where its occurrence would have been most decisive, thus greatly neutralising the force of the argument in favour of the ammonia theory; whilst, on the other hand, this very failure was not only in perfect harmony with, but would be required by, the theory of amidogen bases.

He then proceeds to speak of the recent discovery of methylamine and ethylamine by Wurtz in very remarkable terms, which are deserving of attention at the present time, when it may not be too late to recover fuller information as to the exact manner in which Hofmann was influenced by the work; and in order, also, that the precise relationship of the researches of two such distinguished investigators may be made clear, as well as their relative effect in forming opinion at the time.

Hofmann's eloquent words seem to admit of little doubt as to their meaning, and yet it is a question whether they do not convey a false impression. He says:—

"Yet stronger grounds for the acceptance of the latter view—the amidogen theory—have been afforded by a splendid investigation of M. Wurtz on the compounds of ethers with cyanic acid, which have actually realised a series of substances, anticipated in a most remarkable manner by Liebig on the theoretical ground of his conception of the nature of these compounds. Instances of such anticipation of discovery are so rare that I may be allowed to quote the words in which Liebig predicted, nearly ten years ago, the discovery of M. Wurtz:—'If,' said Liebig, in continuing the development of his ideas respecting the constitution of the organic bases, 'we were able to replace by amidogen the oxygen in the oxides of methyl and ethyl, in the oxides of two basic radicles, we should without the slightest doubt obtain a series of compounds

exhibiting a deportment similar in every respect to that of ammonia. Expressed in symbols, a compound of the formula $C_4H_5 \cdot H_2N = E \cdot Ad$, would be endowed with basic properties.' Now these compounds, imagined in 1840 by Liebig, in illustration of his views, have sprung into existence in 1849 with all the properties assigned to them by that chemist. At the beginning of the present year, M. Wurtz, in investigating the cyanates of ethyl, methyl, and amyl, arrived at the unexpected result that these compounds, when decomposed by potassa, undergo a change analogous to that of cyanic acid. This acid, when treated with potassa, yielding carbonic acid and ammonia, the corresponding ethers were split into carbonic acid and compound ammonias of the exact formula indicated in Liebig's suggestion. It would be difficult to imagine any more brilliant triumph for any theoretical speculation."

If we turn to Hofmann's obituary notice of Wurtz (*Ber.*, 1887, c, 815—996), one of the most brilliant and interesting of the many marvellous biographical sketches of his contemporaries for which chemists will ever be most deeply indebted to him, we find little to help us, and certainly no justification of the statement above quoted *implying* that the discovery of the amines by Wurtz was at the time regarded as affording special grounds for the acceptance of the amidogen theory.

That it excited extraordinary attention there can be no doubt. Hofmann, indeed, tells us that in the whole course of his experience no piece of work ever produced such an impression on the chemical world. Of this we have independent testimony in the fact that Wurtz's papers are reproduced in *Liebig's Annalen* with an editorial postscript, in which it is pointed out that whereas it has been the practice to await the appearance of complete publications before noticing them in the *Annalen*, an exception is made on behalf of Dr. Wurtz's important investigations. Not only are his papers reproduced from the *Comptes rendus*, but also Dumas' report to the Academy, to which a note by Liebig is appended.

If we refer to Wurtz's own statements, we find that, in his brief paper on ethylamine and methylamine (*Compt. rend.*, Feb., 1849, 28, 223), after pointing out that the ammonia compounds, in a measure, come between the inorganic and organic compounds, he remarks that ammonia would be regarded as the simplest and strongest organic base—that it would be considered by all chemists as the type of this numerous class, if it were not separated therefrom by an undoubtedly important characteristic, to which, however, perhaps too much importance had been attached. It contained no carbon. But it appeared that this difference in composition was not sufficient to separate ammonia from the organic bases. He had succeeded in preparing a true organic compound from this alkali by adding the elements either of the hydrocarbon C_2H_2 or C_4H_4 , without depriving it of its character

as a strong base, or even of its most characteristic property—its odour.*

Wurtz clearly regards his discovery as that of *organic* or *compound ammonias*. This is also the view taken by Dumas in his report on the paper; and it is easy to understand that a substance having the properties of aniline, although basic, should have failed to take rank directly with ammonia—consequently, that the discovery of substances *so exactly like ammonia* as are methylamine and ethylamine should have produced a profound effect.

Wurtz, it is true, points out that the compounds he describes may be regarded as methyl and ordinary ether respectively in which one equivalent of oxygen is displaced by one equivalent of amide, NH_2 ; or as ammonia in which one equivalent of hydrogen is displaced by methyl or ethyl—as methyl- and ethyl-amide;† but he does nothing more. Whilst Dumas, in his report, represents the new alkaloids, and a number of others with which he compares them, as conjugated ammonias.

Liebig, indeed, in his editorial note, draws attention to this, and proceeds to recapitulate what he had written 12 years previously in advocacy of the view that the organic bases were amidogen compounds.

It would, therefore, seem that it is justifiable to claim for Hofmann the sole credit for the establishment of the *constitution* of the amines.

The argument which led Hofmann to institute his experiments is stated in the following passage—

“If we give to Liebig’s view the extension of which it naturally admits,

* In his obituary notice of Wurtz (p. 932), Hofmann makes an interesting statement with regard to the discovery of ethylamine, which apparently is not to be met with in Wurtz’s papers. He points out that it is easy, on reading the account given by Wurtz, to underrate the difficulties he encountered in interpreting his results, and that in fact the cyanic ethers had been some considerable time in his hands before he recognised the nature of the change they underwent when acted on by alkalis. Chemists were then under the influence of the recent discovery by Kolbe and Frankland of the formation of ammonia and an acid of the acetic series from the alcoholic cyanides, and it seemed not improbable therefore that a cyanate would give ammonia and an oxygenated acid. Wurtz actually found that on heating ethylic cyanate with alkali, an alkaline gas was evolved, which he for some time regarded as ammonia, but the solution contained only carbonate. For some time he sought in vain, Hofmann tells us, for a compound containing the complementary carbon of the cyanate; at last, one day the alkaline gas took fire and burnt with a luminous flame—like so many other important discoveries, that of ethylamine therefore was partly attributable to accident.

† Later in the paper—and always subsequently—he uses the names *methylamine* and *ethylamine*—qui ont la même termination que ceux des autres alcalis organiques.

and which is demanded by the onward steps of science, we arrive at a more general conception of the nature of the organic bases; amidogen and the amides now presenting themselves to us only as particular instances of the permutations possible among the elements of the primary type ammonia. It seemed but logical to look among the bases for analogues, too, of the imidogen compounds and the nitriles. In other words, it appeared desirable to inquire whether the several equivalents of hydrogen in ammonia could not be replaced, not only by atoms neutralising the basic properties of the original system, but also by elements or groups of elements, not affecting or but slightly modifying the alkaline character of the primary compound. Were this possible, we should arrive at the formation of three classes of organic bases, derived from ammonia by the replacement respectively of one, two, or three equivalents of hydrogen."

He then goes on to say—

"In commencing my experimental inquiry, the first step was to select the particular base which should be the subject of operation, and the radicles whose introduction should be attempted. On the one hand, my previous occupations suggested aniline for the foundation; while, on the other hand, the radicles existing in aniline and its congeners, methylamine, ethylamine, and amylamine, namely phenyl, methyl, ethyl, and amyl, presented themselves as materials for construction."

From this passage it is clear that the investigation was carried out with full knowledge of the discovery made by Wurtz, which is evidence that Hofmann himself at the time did not regard the production of organic ammonias from cyanic ethers as proof of their constitution.

At first the attempt was made to introduce a second equivalent of phenyl into aniline by means of phenol, by heating the two substances together at a high temperature, but unsuccessfully. The action of chloride and bromide of phenyl upon aniline promised a better result, but the difficulties encountered in preparing these compounds deterred him we learn from further pursuing this direction of the inquiry. He was entirely successful, however, in substituting methyl, ethyl and amyl for the remainder of the basic hydrogen in aniline, using for the purpose the bromides or iodides of the radicles.

Self evident as the conversion of an amine by means of an alkyllic bromide or iodide is to us, the issue of such an experiment must have been entirely problematical in 1849, when there were no precedents to rely upon. It is, therefore, to be regretted that no clear indication is given by Hofmann of his reasons for selecting the methods he used, and yet there can be little doubt that the remarkable use which Frankland but a short time before had made of the iodides of methyl and ethyl* had drawn the attention of

* In effecting the isolation of the organic radicles, and in preparing organo-metallic compounds (*J. Chem. Soc.*, June—November, 1849, 2, 263, 297). Frank-

chemists to the value of these compounds as agents, and that the use which Hofmann in turn made of them is traceable to this circumstance; all he tells us, however, is that "the compounds of these radicles (methyl, ethyl, &c.) with chlorine, bromine and iodine appeared to be the most appropriate substances" for the purpose he had in view. Their introduction as substituting agents, however, clearly dates from this time, as indeed, Hofmann himself pointed out a few years afterwards—

"These successive substitutions (of hydrogen in ammonia) were accomplished by the action of ammonia upon the bromides of the alcohol radicles, which since that time have become most valuable agents of substitution in the hands of chemists" (*Proc. Roy. Soc.*, 1858, 9, 151).

Aniline was without difficulty converted into ethyl- and diethylaniline, beyond which stage the substitution could not be carried.* As the passage of ammonia into aniline had been accomplished, as already pointed out, in the course of the experiments Laurent and he had previously made, in which phenol was acted on by ammonia at a high temperature—

"The formation of aniline, ethylaniline, and diethylaniline appeared to have established in a sufficiently satisfactory manner the point of theory in question."

Such are the words in which Hofmann recognises the bearing of his results: the calmness and apparent indifference with which he views his success is almost aggravating.

A true man of action, he at once goes on to remark—

"Still I thought desirable the acquisition of additional facts in support of the position to which this inquiry has conducted me. Thus I have been led to study the action of bromide of ethyl upon several of the derivatives of aniline, and to try whether other alcohol radicles, such as methyl and amyl, would have a similar action; lastly, in order to complete the investigation, I was obliged to leave the amidogen bases altogether, in order to submit the typical ammonia itself to examination."†

land, in the introductory remarks prefacing the first of these papers in his volume of *Experimental Researches* (p. 65), in fact states: "In these experiments the iodides of the alcohol radicles were employed as reagents, I believe for the first time." As we know that, when Frankland's paper was communicated to the Society, "Dr. Hofmann exhibited a specimen of the zinc methyl he had obtained from Dr. Frankland, and demonstrated its spontaneous inflammability," it is evident that his attention had been very specially directed to the work. See also Frankland (*J. Chem. Soc.*, 3, 48).

* It was afterwards recognised that the products obtained on this occasion were not pure substances. The preparation of pure methylaniline and the relative proportions of methyl- and dimethyl-aniline formed on methylating aniline by means of methyl chloride, bromide and iodide were fully gone into by Hofmann many years later (*Ber.*, 1874, 523; 1877, 591).

† The action of ethyl chloride on an alcoholic solution of ammonia was examined

The action of ethyl bromide on chlor- and bromaniline and nitroaniline was first studied; the results obtained were important as throwing light on the constitution of these substitution bases. To quote Hofmann's words—

"The possibility of introducing into these substances* two equivalents of ethyl, shows that they must contain the same amount of basic hydrogen (an expression by which I may be allowed to represent briefly the hydrogen of the ammonia-skeleton) as aniline itself, and hence it is evident that it was the hydrogen of the phenyl which was replaced by chlorine, bromine, and hyponitric acid in the transformation of aniline into its chlorinated, brominated, &c., relatives. The transformation is due to a secondary substitution, affecting the hydrogen in the radicle which replaced the original ammonia-hydrogen."

This seems to have been the only occasion on which the hydrocarbon radicle in aniline in any way engaged Hofmann's attention or excited his curiosity—his interest in aniline seems to have been centred so entirely on its basic properties, his interest in bases to have been so great, that it was long before other problems in any way attracted him.

After preparing a variety of substituted amines from aniline, and showing that it was possible to displace the three hydrogen atoms in ammonia by three different hydrocarbon radicles, Hofmann showed that ammonia could be directly converted, not only into the ethylamine already prepared by Wurtz, but also into a di- and a tri-ethyl derivative; and at once foreseeing the probability "that arseni- etted and phosphoretted hydrogen, which imitate to a certain extent the habits of ammonia," would afford similar derivatives, he announces his intention of extending his researches to these hydrides, a promise which was amply fulfilled in after years.

Hofmann, in the first instance, speaks of the three kinds of base derived from ammonia as *amidogen*, *imidogen* and *nitrile* bases respectively. The terms primary, secondary and tertiary, to which we are so accustomed, appear to have been first used in a lecture which he delivered to the Chemical Society in June, 1858 (*J. Chem. Soc.*, 11, 255), in which the classification of the various derivatives of ammonia—both amines and amides—then known is discussed at great length, reference being also made to the basic derivatives of phosphorus, arsenic and antimony. The closing words of this lecture are worth quoting—

in Hofmann's laboratory by C. E. Groves in 1861 (*J. Chem. Soc.*, 13, 331). He obtained the monethylated compound almost exclusively. Hofmann, working on a large scale, subsequently obtained a mixture of mono-, di-, and tri-ethylamine containing a slight excess of the secondary amine (*Ber.*, 3, 776).

* The statement here made that nitroaniline could be methylated and ethylated was corrected in a later paper (*Roy. Soc. Proc.*, 1862, 12, 639).

"In the preceding paragraphs I have endeavoured to give an outline of the chemical history of the type ammonia, such as it exhibits itself at the present moment. No department of chemistry, perhaps, reflects in a more salient manner the rapid progress of science during the last quarter of a century. Nearly all the bodies mentioned in this paper were discovered during that period; nine-tenths, in fact, the very compounds which have most assisted in the elaboration of our theoretical views, are the fruits of the last 10 years. Though much has been achieved, more is left to be done. But even now, while so many known substances remain to be finally grouped and classified, and while countless groups and classes remain to be discovered, yet the general features of the system are distinctly perceptible, and the time is rapidly approaching when, losing sight of the chaotic mass of overwhelming detail, the eye may rest with complacency upon the simple beauty of the law which governs the construction of the bodies belonging to the type of ammonia."

When we recollect how entirely we owe to Hofmann the establishment of the "simple beauty of the law" governing the constitution of amines generally, this passage may justly be selected as a fit epitaph to attach to his work.

The monamines were largely used by him in subsequent investigations, as will appear in the sequel, and therefore, in concluding the account of his researches of the monamines, it will only be necessary to refer here to the process which he devised of separating the ethylamines, and also to his proposals for effecting the diagnosis of amines.

Although they differ considerably in boiling point, it is impossible to separate the ethylamines by fractional distillation.* The "simple and elegant process," as he himself originally termed it, devised by Hofmann (*Proc. Roy. Soc.*, Nov., 1860, xi, 66) is based on the observation that when submitted to the action of ethylic oxalate, ethylamine is converted into diethyloxamide, a crystalline substance, only sparingly soluble in water; whilst diethylamine yields ethylic ethyloxamate, a liquid boiling at a high temperature; triethylamine remaining unchanged. Hence, after subjecting the mixture to the action of the oxalate, it is possible to separate the tertiary base by distillation, and to mechanically separate the crystalline amide from the oily oxamate; the amide may then be purified by recrystallisation from boiling water, and distilled with alkali, the oxamate being similarly treated after separating the dissolved oxamide by cooling to 0°, and then fractionally distilling the liquid.

* The boiling points, &c., of the various methyl- and ethyl-amines were determined by Hofmann in 1889 (*Ber.*, 699), with the aid of large quantities of purified material placed at his disposal by Kahlbaum. In describing his results he states that the experience gained in working on the large scale had proved that these amines were best prepared by his original method.

It was subsequently pointed out (*ibid.*, p. 526) that a simpler and more perfect separation of the oxamide and oxamate might be effected by submitting the mixture at once to the action of boiling water, when diethyloxamide dissolves, the oxamate remaining as an insoluble layer floating upon the hot solution. Hofmann re-examined the process ten years later, when the opportunity occurred to prepare the ethylamines on a large scale with the aid of ethyl chloride obtained as a bye-product in the preparation of chloral (*Ber.*, 3, 109, 776). The criticisms to which the method had been subjected were considered, and a full account was given of the manner of operating which experience had shown to be the best.

Provided that sufficient material be at disposal, the diagnosis of the amines is easily effected, following the indications afforded by Hofmann's inquiry, by ascertaining the number of methyl or ethyl groups which can be introduced in place of hydrogen, but the method involves the analysis of the product. A qualitative method of perfectly general application in the case of primary, but of restricted application in the case of secondary amines, was proposed by him in 1870 (*Ber.*, 3, 767), after he had discovered the isonitriles.

All primary amines yield the corresponding isonitrile when warmed with alcoholic potash and chloroform, and these nitriles are all possessed of intolerable odours. On the other hand, both primary and secondary paraffinoid amines form thiocarbamates with carbon bisulphide, and these are converted by mercuric chloride into mustard oils, which are also characterised by their evil odours.

By reversing the test, the primary amines become remarkably delicate tests of chloroform; it is possible, for example, to detect with certainty 1 part of chloroform in 5000 to 6000 parts of alcohol by means of aniline.

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In the second memoir, entitled "Researches into the Molecular Constitution of the Organic Bases," published in the *Phil. Trans.* of the Royal Society (1851, ii, 357; Abstr., *J. Chem. Soc.*), Hofmann considers "the history of a new group of alkaloids, which, although intimately connected (with the amines) by their origin, differ from them altogether by their properties, and especially in *not being volatile*." After having succeeded, he tells us, in replacing, step by step, one, two, or three equivalents of hydrogen in ammonia by a corresponding number of compound atoms, the question arose whether the agent by which these changes were effected would exert a still further influence on the last product of the action. In order to decide this question by experiment, he submitted two nitrile bases, diethylaniline and triethylamine, to the prolonged action of bromide of ethyl. These experiments did not lead to perfectly decisive results. It was evident

that in these cases an action ensued. . . . No doubt, however, could be entertained as to this action being altogether different from the preceding stages of the process.

A mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed up in a tube, solidified after several hours ebullition, the crystals consisting chiefly of the fibrous hydrobromide of triethylamine, with which, however, a certain quantity of white, opaque, granular crystals was invariably mixed. Anhydrous materials were therefore used, in the hope of increasing the quantity of this latter substance, but the progress of the action was found to be retarded in a most remarkable manner by this variation, days elapsing before the conversion was completed. But the difficulty thus met with was soon overcome by using iodide instead of bromide of ethyl, action taking place almost instantaneously on warming a mixture of the anhydrous substances, the product—as every chemical tyro now knows—being an iodide formed by the direct combination of the triethylamine with the ethyl iodide.

The properties of the iodide thus produced are so remarkable, there is still so much that requires explanation in connection with such compounds, that the account Hofmann originally gave may be quoted almost verbally with advantage, both because it is historically full of interest, and in order that attention may be directed to a subject which is rarely more than superficially noticed in our textbooks. It is in no way surprising that he should remark—

“I confess I had not anticipated the possibility of the existence of (such) a compound; it appeared at the first glance in direct opposition to the theoretical view repeatedly referred to. For if it was possible to decompose the new iodide by potassa, just as the preceding iodides, . . . if it was possible to separate from this substance a new volatile base analogous to the preceding ethylated alkaloids, there was no reason why the process of ethylation should cease with the fourth equivalent of ethyl. On the contrary, it then appeared more than probable that the formations of ethylamine, diethylamine, and triethylamine, far from being due to the successive replacement of the various equivalents of hydrogen in ammonia, were rather to be considered as special instances of a far more general tendency of carbon and hydrogen to accumulate in organic substances.

“The eagerness with which I submitted this question to the test of experiment may be readily imagined”—Indeed, it may!—“On adding potassa to a solution of the iodine compound in water, the liquid solidified at once into a crystalline mass, which I took of course for the base existing in the iodide; analysis, however, soon showed that the substance thus precipitated is nothing but the iodide itself, which is less soluble in an alkaline solution than in pure water. The iodide was now distilled with a very concentrated solution of potassa for several hours; but during this time nothing but pure water passed over. The solution in the retort solidified on cooling to crystals of the unchanged iodide. When the solution of the iodide in

potassa had become very concentrated, it separated into two layers, an aqueous one and an oily one, which floated on the surface. But even now no decomposition had been induced, the oily stratum solidifying on cooling into a crystalline cake of iodide perfectly unaltered. It was only when the liquid was evaporated to dryness that a change took place; but then the change was no longer due to the action of the potassa, but to the influence of heat, and in no way differed from the decomposition which the crystals undergo when heated alone" (into triethylamine and ethyl iodide).

"The deportment with potassa of the new iodine compound altogether precludes the idea of considering it as an analogue of the hydriodides of ethylamine, diethylamine, and triethylamine, all of which are readily decomposed under the influence of the alkalis.

"However, the iodine, though it cannot be eliminated from the crystals by the alkalis, may be separated with the greatest facility by silver salts; in fact, the nitrate, the sulphate, the oxide of silver behave with the iodine compound exactly as with iodide of potassium or sodium. . . . In fact, the molecular group combined with iodine, in the compound under examination, behaves like sodium or potassium; it is a true organic metal in all its bearings. For this metal, I propose, on the ground of its formation and composition, the name tetrethylammonium (*τέτρα*), which implies that it is built up by the intimate union of nitrogen with four equivalents of the hypothetical hydrocarbon called ethyl, and that it may be viewed as ammonium, in which the whole of the hydrogen is replaced by an equivalent proportion of the above hydrocarbon."

"The new crystalline compound, according to this mode of viewing it, must be considered as iodide of tetrethylammonium, and its formation takes place in consequence of a transposition of the elements, which is perfectly analogous to that assumed by the followers of the ammonium theory in the formation of iodide of ammonium from ammonia and hydriodic acid."

We have here a complete statement of the ammonium theory of the constitution of such iodides and of analogous compounds, accepted in its entirety from the time of Hofmann's experiments up to the present day. But it is important to note that he explicitly guarded himself when putting this view forward by stating—

"I will not enter here into the merits of the ammonium theory; the question whether this mode of representing the constitution of the ammonia salts be correct or not may be left out of consideration for the present. The view I have taken of the new compound, and which I readily admit must stand and fall with the ammonium theory, has the great advantage of closely assimilating these substances to the compounds of mineral chemistry, whereby the nomenclature is essentially facilitated."

In the memoir under consideration there is much else that is of importance from many points of view. The iodide having been described, a full account is given of the remarkable properties of the hydrate formed on digesting it with silver oxide; and the extraordinary resemblance which this compound bears to the fixed caustic

alkalis is established in the most thorough manner possible. Among the properties of this substance to which reference is made, one deserves mention as somewhat singular, namely, the formation of a crystalline precipitate of the corresponding iodide on adding a concentrated solution of the tetrethylammonium hydrate to an alkaline solution of iodide of potassium. This phenomenon, it is pointed out, is due to the insolubility of the iodide in alkaline solutions, and not to the new base possessing a greater affinity for iodine than potassium. Another illustration of the readiness with which the iodide is formed is afforded by its production on boiling the hydrate (a concentrated solution) with ethyl iodide, the latter being converted into alcohol.

The memoir also contains a description of a number of mixed ammonium compounds analogous to the tetrethylammonium derivatives, prepared, for example, by combining methyl or amyl iodides with triethylamine, or from other nitrile bases than this last, as well as of the tetramethyl and tetramyl compounds. These were all found to exhibit the closest resemblance in their properties.

The behaviour of the hydrates is deserving of special mention. When a solution of tetrethylammonium hydrate ($\text{NEt}_4\cdot\text{OH}$) is concentrated *in vacuo*, crystals are obtained of a hydrated compound. On evaporating such a solution on the water bath, decomposition sets in even before the water is completely driven off, the hydrate being resolved into triethylamine, ethylene and water, thus affording a means of preparing pure triethylamine. Hofmann also examined the behaviour of the amyltriethyl-, of the methyldiethylamyl-, and of the phenyltriethyl-ammonium hydrates, and in each case found that ethylene was the gas evolved. That the amyltriethyl compound should undergo decomposition in this way is somewhat remarkable, especially as the tetramyl derivative is resolved into triamylamine, water and amylene, and it is therefore noteworthy that the amyl compound is stated to be far less easily decomposed than the corresponding tetrethylammonium hydrate. Naturally, the tetramethylated compound was investigated, in the hope that it would afford methylene, but no gas was obtained from it; the precise nature of the change which it underwent was not determined.

Hofmann makes an important use of these facts, and of the properties of the substituted ammonium compounds generally, in discussing the constitution of the ammonia salts. The arguments he advanced nearly fifty years ago are still adopted at the present day, and, notwithstanding the attention since devoted to the subject, the problem remains much in the condition in which it was left by him—it will probably not be going too far to say entirely unsettled, conclusive in its favour though the arguments appear to be; nor is this strange, as

the settlement of the most difficult problem in chemistry is involved in its solution.

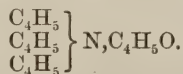
Several passages from this part of Hofmann's memoir merit reproduction here, if only as a model of lucid and philosophical statement.

"Without reproducing all the arguments brought forward by the supporters of the various theories (regarding the constitution of the ammonia salts), we may remember (he says) that, irrespectively of the impossibility of isolating ammonium itself, the instability of its oxide has been adduced as one of the most important objections against the assumption of the ammonium theory as originally suggested by *Ampère*, and subsequently elaborated by *Berzelius*. It deserves to be noticed that Berzelius expressly states that he considers the solution of ammonia gas in water as a solution of the hydrated oxide of ammonium. This idea, which is but a logical conclusion from the generalisation of the facts, is discountenanced to a certain extent by the chemical and physical character of this solution. Everybody knows that, even at the common temperature this liquid splits again into water and ammonia, while it still exhibits the character of the latter in so marked a manner as almost to preclude the idea that it had undergone as essential a change as the transformation into oxide of ammonium necessarily must be. Under these circumstances, some interest is attached to the discovery of a series of compound bases, corresponding in their composition to hydrated oxide of ammonium, from which they differ only by containing methyl, &c., in the place of hydrogen, and exhibiting a deportment which agrees much better with the anticipated character of such compounds as suggested by analogy. Here we find a very marked difference between the properties of the compound ammonia, and those of the ammonium oxide belonging to it; in the latter, we observe no longer any feature which could possibly betray the presence of the former; all their habits, volatility, odour, taste, &c., are totally changed; there is a difference between the two groups which is not inferior to that between ammonia and potassa. The solutions of the two oxides may be boiled for hours without the slightest quantity of the corresponding ammonia being disengaged; several of these oxides, containing more or less water of constitution or crystallisation, may actually be obtained in the dry state. It is evident that the arguments mentioned above, as adduced in refutation of the ammonium theory, cannot well be raised against the compound ammoniums. But who could deny the parallelism of these substances with the Berzelian type—with the oxide of ammonium?

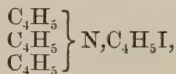
"Again, many have found it difficult to conceive, that in the combination of ammonia with hydrochloric or hydrobromic acid, the hydrogen of the latter should leave the chlorine and bromine, for which it is known to possess so powerful an affinity, in order to unite with ammonia, converting it into ammonium. And they were the less inclined to admit of such a disposition of the elements, as every day's experience showed that the alleged chloride or bromide of ammonium was incapable of exchanging oxygen for chlorine or bromine, without losing the additional equivalent of hydrogen again in the form of water. In other terms, the decomposition of sal-ammoniac by lime, into chloride of calcium, ammonia gas, and water induced them to con-

sider this salt as a compound of ammonia and hydrochloric acid ; for, in the conception of the ammonia theory, we should have to assume in this decomposition *two* consecutive changes, the transformation of the chloride into oxide, and the subsequent splitting of the latter into ammoniacal gas and water. I readily admit that the latter view is less simple, but I am inclined to think that this slight inconvenience is altogether overruled by the general advantages of the ammonium theory, especially for the purposes of instruction, by the facility with which it accounts for all phenomena of transposition and substitution, and by the simple explanation it gives of the isomorphism of the potassium and ammonium compounds, which will always be the firmest foundation of this theory. On the other hand, we have to inquire which of the two views comes nearest to the truth, and here a comparative consideration of the deportments exhibited by the compound ammoniums may be of some interest. In many respects their properties are more clearly pronounced ; and their behaviour is explicit and unequivocal in those very points in which the typical ammonium leaves room for speculation. In the combination of triethylamine with bromide or iodide of ethyl, it is no longer a matter of doubt whether the ethyl leaves the iodine in order to unite more intimately with the triethylamine, for we see that the new iodide thus produced is capable of exchanging its iodine for oxygen without the newly formed oxide suffering immediate decomposition, as is the case with oxide of ammonium. On the contrary, we find this new oxide endowed with remarkable stability ; although under the influence of heat it is liable to the same change which befalls the oxide of ammonium, its corresponding ammonia being reproduced. Here then in the decomposition of iodide of tetrethylammonium by metallic oxides, we are obliged by irresistible evidence to acknowledge these very two stages, the assumption of which in the analogous change of iodide of ammonium appeared to us deficient in simplicity and probability.

"The conception of ammonium does not in any way imply the notion that the different hydrogen atoms united with nitrogen in the molecules of the compound metal retain their position in the molecular system with equal persistency. We are forced by unequivocal facts to admit that the fourth atom of hydrogen is in a peculiar state of mobility, and it is on the facility with which this fourth atom is dislodged from its position that one of the foundations of the ammonia theory rests. In the compound ammoniums, the mobility of the fourth atom of hydrogen, or the hydrocarbon replacing it, still prevails, although less so than in the type itself. The decomposition of the ammonium bases under the influence of heat is particularly instructive in this respect ; oxide of tetrethylammonium loses the fourth equivalent of ethyl in the form of olefiant gas and water ; and this deportment might be graphically indicated by writing the formula of this compound in accordance with the ammonia theory, namely, thus

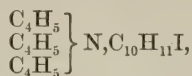


"The iodide, accordingly, would be represented by the formula

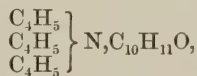


an expression which is, moreover, in perfect harmony with the mode in which this compound is produced, namely, by the direct union of iodide of ethyl with triethylamine.

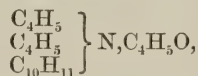
"But now we combine the triethylamine with iodide of amyl, whereby the iodide



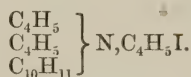
is formed which, as we have seen in the preceding pages, may be converted without difficulty into the corresponding oxide; this oxide, however, cannot possibly be considered as



for the disengagement of olefiant gas, under the influence of heat, proves to us that it is an ethyl atom, which in this compound occupies the supplemental position, if I may so call it, as represented in the formula



and that the iodide, which is not likely to differ in its constitution from the oxide, has likewise to be represented by the formula



"The preceding considerations clearly show, that, whatever the actual disposition of the molecules in ammonium or its congeners may be, the atoms rearrange themselves whenever the fourth equivalent of hydrogen, or of its substitute, joins the compound.

"This rearrangement, so evident in the ammonium bases containing various hydrocarbons, may be traced, moreover, in the lower ethyl bases in a very obvious manner. For as long as there is any basic hydrogen present in the ammonia skeleton, this hydrogen assumes what I have previously called the supplemental position, whenever the ammonia passes into the state of ammonium by the accession of a radicle. Bromide of ethylammonium, formed by the combination of ammonia with bromide of ethyl, when decomposed by a metallic oxide, yields ethylammonia, water, and a metallic bromide; the oxide of ethylammonium formed in the first instance being decomposed like oxide of ammonium itself. It is this very transposition which we are in the habit of representing by the equation



Later researches have shown that the argument used by Hofmann, based on the behaviour of the hydroxides, is, after all, of limited value; it was first pointed out by Lossen, in 1876 (*Liebig's Annalen*, 1876, **181**, 364), that whereas the ethylated hydroxides, as a rule, lose ethylene and water when distilled, whatever the other groups

may be, in the case of the chlorides, if methyl be present, methyl chloride is usually split off.

Collie and Schryver, after studying the effect of heat on a number of mixed ammonium compounds, came to the conclusion, however, that when a mixed quaternary ammonium chloride (made from trimethylamine or triethylamine) is heated, *a mixed tertiary amine is always produced*. But the actual amount formed varies very considerably in the case of different compounds, the only product from trimethylphenylammonium chloride, for example, being dimethylphenylamine, whilst trimethylamine is chiefly formed when allyl- and isopropyltrimethylammonium compounds are decomposed. The behaviour of the chlorides and hydroxides is also sometimes diverse: thus, whilst trimethylbenzylammonium chloride yields dimethylbenzylamine and methyl chloride, its hydroxide is resolved into trimethylamine and benzyl alcohol; but methyltriethylammonium chloride yields triethylamine, whilst the hydroxide is converted into methyldiethylamine.

The belief has gradually grown up, however, that nitrogen acts as a pentad in the ammonium compounds, and that no distinction is to be drawn such as is implied in Hofmann's reference to a supplemental position, although the evidence that this is the case is still incomplete. An important series of experiments has been made by V. Meyer and Lecco directly with the object of ascertaining whether isomeric compounds can be formed by combining, on the one hand, dimethylethylamine with ethyl iodide, and, on the other, diethylmethylamine with methyl iodide; finding the products to be identical, they came to the conclusion that the ammonium compounds are to be regarded as atomic, and not as molecular, compounds (*Liebig's Annalen*, 1876, **180**, 173).

But Lossen has pointed out that their results do not necessarily establish the correctness of their conclusion. It is possible, he thinks, that an exchange of radicles may take place during the formation of the ammonium compound. Moreover, he does not regard the fact that the products are crystallographically identical as proof that they are actually identical in structure, his argument being that two compounds such as $\text{NMe}_2\text{Et}\cdot\text{EtI}$ and $\text{NEt}_2\text{Me}\cdot\text{MeI}$ would be so similar that they would probably crystallise in isomorphous forms (*Liebig's Annalen*, 1876, **181**, 364).

On mathematical grounds, the five valencies of a nitrogen atom cannot be all similar. In the case of compounds of the type $\text{NRR}'_3\text{Cl}$ it may be assumed, however, that the five radicles are distributed upon a sphere, and either that their mutual position is changeable, and therefore no isomerism is possible; or that the positions of the five groups are fixed, and that at least two isomerides are possible. In the case of the simpler derivatives of ammonium chloride contain-

ing hydrogen or methyl, the former view seems correct; but, in the case of derivatives containing more complicated radicles, it might be expected that, owing to their mass and size, these would not change their mutual positions so readily as do hydrogen or methyl. Le Bel is of opinion that isomerism of this kind is recognisable (*Compt. rend.*, 1890, **110**, 145). On examining a whole series of cubic mixed ammonium platinichlorides, and determining the stage at which cubic symmetry vanished, he found that whilst the trimethylpropylammonium platinichloride was still cubic, the homologous isobutyl compound was dimorphous—at first crystallising in long, highly doubly refracting forms, which change into feebly doubly refracting octahedra closely resembling cubic crystals. The chlorides from these platinichlorides were also different (*ibid.*, 1893, **116**, 513). Collie and Schryver came to somewhat similar conclusions in the case of methyl-diethylisoamylplatinichloride.

Moreover, Le Bel has stated that it is possible to prepare optically active isobutylpropylethylammonium chloride (*Compt. rend.*, 1891, **112**, 724).

It is clear, therefore, that the last word has not yet been said on the subject.

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About eight years after the publication of his researches on the ammonium compounds, Hofmann, in conjunction with Cahours, brought under the notice of the Royal Society an account of their researches on the phosphorus bases (*Phil. Trans.*, June, 1857, 575), in which they described the now familiar method of preparing trimethyl- and triethyl-phosphine by means of Frankland's zinc methyl and zinc ethyl* and phosphorus trichloride, as well as a number of phosphine derivatives, and also several phosphonium compounds corresponding in the closest manner possible to the ammonium compounds.

The history of this investigation may be traced by reference to a paper presented to the French Academy by Cahours in Hofmann's and his own names in November, 1855 (*Compt. rend.*, **41**, 831).

Hofmann, at the close of his great memoir on the amines, had not failed to draw attention to the compound prepared by Thénard in 1845 from calcium phosphide and methyl chloride as being probably the analogue of trimethylamine. Cahours, after referring to Thénard's work, points out that the subsequent discovery of stibethyl by Löwig and Schweitzer, and that of the compound ammonias by Hofmann, afforded proof that the hydrogen in ammonia and its analogues may be displaced by methyl, &c., without the loss by these

* The writer has been told by Dr. Frankland that at Hofmann's request he prepared the zinc ethyl used in the first experiments made to test the method.

hydrides of their basic properties; nay, more, that in the case of arsenic and antimony the basic properties become actually enhanced. The discovery of the tetramethyl bases of Hofmann, followed by that of the corresponding arsenic and antimony bases made simultaneously by Cahours and Riche on the one hand and Landolt on the other, had shown, moreover, that it was possible to go further and displace the four hydrogen atoms in ammonium by alcohol radicles, and that corresponding compounds of arsenic and antimony could exist. There remained but the blank between the compounds of nitrogen and those of arsenic to be filled up; and to supply this want, therefore, during a stay of a month in London, he had undertaken the study of the phosphorus compounds with Hofmann.

The monograph published by the Royal Society was the outcome of the inquiry thus initiated, which was carried out with the assistance of Dr. Leibius and Messrs. Perkin and C. Hofmann. Trimethyl- and triethyl-phosphine are fully described in it, and their perfect analogy with triethylamine demonstrated by their behaviour with the iodides of methyl, ethyl and amyl. Tetrethylphosphonium iodide is shown to resemble the corresponding ammonium iodide, and to be extremely soluble in water, but precipitable by potash. The corresponding hydroxide, whilst behaving exactly like caustic potash, and therefore resembling tetrethylammonium hydroxide, differs—it is pointed out—from the latter in its behaviour on heating, owing to the affinity of phosphorus for oxygen coming into play, yielding ethane and triethylphosphine oxide.* Lastly, attention is drawn to the extraordinary affinity of triethylphosphine to sulphur and selenium.

The analogies presented by the four elements—nitrogen, phosphorus, arsenic, antimony—as well as their peculiarities are pointed out by Hofmann and Cahours in this memoir with a clearness and precision before unknown, and in a manner which leaves no word to be said even at the present day.

The analogy between the four elements, they remark,

“Is particularly manifest in the compounds belonging to the ammonium type. In these remarkable bodies, nitrogen, phosphorus, arsenic, and antimony appear to play absolutely the same part. It is more especially in the oxides of these compound metals that analogy of composition induces a perfect identity in properties, and, indeed, of very salient properties which may be traced in almost every direction. If we were satisfied with the study of the reactions of these bodies, we should never suspect, in compounds exhibiting such a close similarity of properties, the presence of elements so

* The manner in which a number of phosphonium derivatives decompose when heated has been since carefully studied by Letts and Collie and by Collie (*Chem. Soc. Trans.*, 1888, 714).

dissimilar as nitrogen, phosphorus, arsenic, and antimony; they might, moreover, be confounded with potassa and soda, by which they are scarcely surpassed in alkaline power. Only the deportment of the hydrated oxides, under the influence of heat, distinguishes the derivatives of nitrogen from the corresponding terms of the phosphorus, arsenic, and antimony series.

"If we regard, on the other hand, the compounds belonging to the ammonia type, we observe that the electro-positive character of the substances gradually rises in intensity from the nitrogen to the antimony compounds. Thus trimethylamine and triethylamine are not capable of uniting with oxygen, chlorine, bromine, and iodine; a power which the corresponding terms of the phosphorus, arsenic, and antimony series possess in a high degree. Triethylamine unites with the acids producing compounds of the formula



"The corresponding compounds in the arsenic and antimony series do not exist; at all events, chemists have not yet succeeded in preparing them. Triethylamine and triethylstibine only combine directly with oxygen, chlorine, sulphur, &c., producing saline bodies which have the composition respectively



"In the phosphorus series, lastly, two classes are represented. Triethylphosphine not only forms compounds analogous to the salts of triethylamine, but also the terms corresponding to the binoxides of triethylamine and triethylstibine. We have, in the first place, the terms



and, in the second place, compounds of the formulæ



"The phosphorus compounds, accordingly, hold a position intermediate between the nitrogen compounds, on the one hand, and the arsenic and antimony series on the other. It cannot, however, be denied that the phosphorus compounds stand closer to the arsenic and antimony series than to the nitrogen group.

"Ammonia is a powerful alkali; phosphoretted hydrogen only unites with hydrobromic and hydriodic acids, whilst in arseniетted and antimonетted hydrogen the power of combining with acids has altogether disappeared. In these hydrogen compounds the gradation of properties is, indeed, much more marked than in their trimethylated and triethylated derivatives. On comparing the terminal points of the series, ammonia and antimonетted hydrogen, we cannot fail to be struck by the dissimilarity of properties which at the first glance appears to limit the analogy of the two compounds to a mere parallelism of composition. In the methylated and ethylated derivatives of these compounds, the intensity of the chemical tendencies in general is so much raised that the gradation is no longer perceptible to the same extent."

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Hofmann devoted much attention to the study of phosphine derivatives during the three years following the publication of the

paper by Cahours and himself, presenting no fewer than 12 communications to the Royal Society, which were finally embodied in three memoirs communicated to the Society in June, 1860, entitled "Contributions to the History of the Phosphorus Bases"* (*Phil. Trans.*, 1860, 408—533). It is noteworthy that these contain accounts of a large number of crystallographic determinations by Quintino Sella, whom Hofmann terms "My friend, the celebrated crystallographer of Turin," and whose life he afterwards portrayed in a lengthy essay, perhaps the most remarkable and masterly of the numerous biographical notices of which he was the author; his inimitable skill in such matters is especially obvious in this case, as the subject of his memoir was not a chemist; yet he produced an account full of interest to chemists, which must rank as an enduring memorial of his remarkable versatility and literary power.

The first of the memoirs under consideration deals with the specific properties of triethylphosphine, which Hofmann speaks of as "a body in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness."

Having recounted his experience of the best method of preparing the phosphine, its oxide is fully considered. This compound exhibits in general but a slight tendency to unite with other substances; nevertheless, we are told, it affords a crystalline compound with iodide of zinc, for example, $[(C_2H_5)_3PO]_2ZnI_2$, which, strange to say, is formed in presence of a large excess of hydriodic and even of hydrochloric acid. When the anhydrous oxide is added to a concentrated solution of platinic chloride in absolute alcohol, a crystalline platinum compound is precipitated which Hofmann represents by the remarkable formula $[(C_2H_5)_3PO]_3(C_2H_5)_3P_2Cl_2PtCl_4$, but to which Letts and Collie, who have prepared a similar compound from tribenzylphosphine oxide, assign the formula $4(Et_3PO), 2HCl, PtCl_4$ (*Roy. Soc. Edin. Trans.*, 30, 207). A peculiar crystalline oxychloride, $(C_2H_5)_3PO, (C_2H_5)_3P_2Cl_2$, is said to be formed on subjecting the oxide to the action of gaseous hydrogen chloride.

The observations of most interest in the paper relate to the interaction of sulphur compounds and triethylphosphine. Although sulphur unites with triethylphosphine with the greatest readiness, and sulphide of nitrogen is instantly deprived of its sulphur by its action, sulphuretted hydrogen is without action, even in presence of air, the attraction of the phosphine for oxygen preventing the oxidation of the hydride. Mercaptan alone is also without action, but in presence of oxygen converts the phosphine into the sulphide,

* Hofmann uses the new notation for the first time in these memoirs. The preliminary communications which had been published in the Proceedings were in the old notation.

the mercaptan being reciprocally converted into alcohol. As triethylphosphine oxide and mercaptan may be placed under the most varied conditions without yielding a trace of triethylphosphine sulphide, we have to suppose, Hofmann points out, that the mercaptan interchanges its sulphur with the oxygen of the phosphine oxide only at the instant of formation of the latter; or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

All attempts to displace the oxygen in triethylphosphine oxide by sulphur were unsuccessful, although the opposite change was readily effected. The different degrees of stability which characterise the oxide and sulphide are also strikingly illustrated by their behaviour towards sodium, from which the oxide may be distilled without suffering alteration, although the sulphide is reduced by it with the greatest facility to triethylphosphine.

The most remarkable of all the phosphine derivatives prepared by Hofmann, however, is the beautiful red crystalline compound of triethylphosphine and carbon bisulphide, $\text{Et}_3\text{P}\cdot\text{CS}_2$, which is immediately formed on bringing the two substances together*—a compound which possesses the character of a weak base. It is noteworthy that no corresponding compound is obtainable from either triethylamine or triethylstibine, or from primary or secondary phosphines, although the last two are acted on by the bisulphide.

The bisulphide compound exhibits a remarkable tendency to pass into sulphide of triethylphosphine, as, for instance, when its alcoholic solution is mixed with silver nitrate. It also decomposes in contact with water, yielding the sulphide as principal product, together with the oxide, carbon bisulphide and triethylmethylphosphonium hydrate. A small quantity of a yellow crystalline substance is also formed, the composition of which is represented by the formula $\text{C}_8\text{H}_{17}\text{PS}_3$; the production of this compound was traced by Hofmann to the action of sulphuretted hydrogen, and he succeeded in preparing considerable quantities of it by digesting the red crystals with a saturated solution of sulphuretted hydrogen at 100° . It may be recrystallised from boiling absolute alcohol, although not without a certain loss; when boiled with water, it is entirely decomposed, carbon bisulphide being evolved, the solution becoming faintly alkaline. On neutralising the liquid with hydriodic acid, a sparingly soluble crystalline iodide is

* This substance is produced with such facility, and its appearance is so characteristic that its formation may be used as a test either for carbon bisulphide or for the tertiary phosphine; it is easy, as Hofmann showed, to demonstrate the presence of carbon bisulphide in coal gas with its aid, and even to use it as a means of estimating minute quantities of the bisulphide (*Ber.*, 1880, 13, 1732).

Hofmann's researches on the phosphine and phosphonium compounds, which followed his investigations of the monamines and the corresponding ammonium compounds, and which, as we have seen, were the direct logical outcome of these inquiries, also largely paved the way for the successful examination of the more complex derivatives obtained with the aid of compounds like ethylene bromide. The second of his three memoirs on the phosphorus bases, in fact, deals with the products obtained from this haloid and triethylphosphine, and is of particular interest, as the results were of importance in aiding him to place beyond question the nature of the interactions involved in the formation of the polyammonias generally.

His reasons for studying "polyacid" bases are stated with characteristic clearness in the opening paragraphs of the paper, and it will be of interest to quote them, as they serve to show the manner in which he was led by concurrent discoveries to thus extend his inquiries—

"In surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot help recognising as one of the most valuable amongst their acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the chemical researches of Graham and Liebig on the polybasic acids, and afterwards extended and generalised by the experiments of Gerhardt and Williamson, it has acquired in Berthelot's beautiful investigation of glycerin a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. Buff, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation ; until, in the brilliant experimental researches of Wurtz on the diatomic alcohols, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

"Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids, and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies ; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination."

After remarking that—

"Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained,"

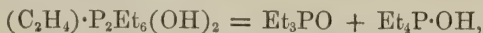
Hofmann proceeds to point out what products might be formed from ethylene bromide and ammonia or the amines; he then refers to the experimental difficulties involved in the separation and recognition of all the products of such complex interactions, and finally remarks—

“Nevertheless, the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus series, using, instead of triethylamine, the corresponding phosphorus base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness, and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality such as I have never observed in any similar reaction among bodies of the nitrogen series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus series.”

The primary products of the interaction of ethylene dibromide and triethylphosphine were found to be two in number, the one being *bromethyltriethylphosphonium bromide*, $(\text{BrC}_2\text{H}_4)\text{PEt}_3\text{Br}$, the other, *ethylenehexethyldiphosphoniumdibromide*, $(\text{C}_2\text{H}_4)\text{P}_2\text{Et}_6\text{Br}_2$. The former behaves in an interesting manner with silver salts and silver oxide, the oxide causing the displacement of the whole of its bromine by hydroxyl, converting it into hydroxyethyltriethylphosphonium hydrate, the compound represented by the formula, $(\text{HO}\cdot\text{C}_2\text{H}_4)\cdot\text{PEt}_3\cdot\text{OH}$; whereas a salt, such as silver acetate, whilst readily exercising a similar effect on the one atom of bromine, more slowly induces the separation of the other atom of bromine together with an atom of hydrogen, thus giving rise to a vinyltriethylphosphonium hydrate, $\text{C}_2\text{H}_3\cdot\text{PEt}_3\cdot\text{OH}$. The bromide corresponding to this latter hydrate may be formed directly from the bromethyl bromide by heating it.

The diphosphonium compounds closely resemble the phosphonium compounds. The diiodide, for example, Hofmann points out, like most diphosphonium compounds, exhibits great stability; it melts at 231° , without undergoing the slightest change, although it is decomposed when more strongly heated over an open flame. A remarkable character of this salt is its insolubility in a moderately concentrated solution of potash; its solution, like those of the diphosphonium salts in general, is perfectly neutral. The hydrate commences to decompose at 160° , and, on raising the temperature gradually to 250° , the

whole passes over in the form of liquid and gaseous products. Hofmann arrived at the conclusion that it undergoes two principal transformations, a portion yielding triethylphosphine oxide and tetrethylphosphonium hydrate,



of which the latter is ultimately resolved into triethylphosphine oxide and ethane; whilst a second portion is resolved into triethylphosphine and hydroxyethyltriethylphosphonium hydrate,



and of these the latter is at least in part converted into water and vinyltriethylphosphonium hydrate, which in turn becomes converted into ethylene and triethylphosphine oxide. A peculiar (?) molecular change precedes the actual decomposition of the dihydrate, a point being soon reached during the distillation when, on testing with platinum chloride, instead of the slightly crystalline precipitate insoluble in dilute hydrochloric acid, characteristic of the original substance, an amorphous, generally dingy yellow, precipitate is obtained, which immediately dissolves on adding a few drops of dilute hydrochloric acid. This amorphous precipitate, however, has the same composition as the crystalline ethylene diphosphonium platini-chloride.

Having found that bromethyltriethylphosphonium bromide was readily converted into ethylenhexethyldiphosphonium dibromide by the addition of triethylphosphine, Hofmann prepared a large number of mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic and arsenic-nitrogen series by subjecting the bromethyl bromide to the action of ammonia and various monamines, mon-arsines, &c.; an account is given of these in the third memoir on the phosphorus bases. The compounds described resemble in the closest manner possible those produced from triethylphosphine alone; thus the hydrates of the base prepared from the bromethylphosphonium bromide and ammonia instead of behaving as an ammonium hydrate when distilled, is resolved into ammonia, water and vinyltriethylphosphonium hydrate. Hofmann also failed, in like manner, in obtaining an ethylenetetrethylphosphamine from the phosphammonium compound formed with the aid of ethylamine.

Some peculiarities are brought under notice in this memoir which deserve attention. Thus it is pointed out, that whereas trimethylamine readily combines with the bromethylated triethylphosphonium bromide, triethylamine, acting in presence of water (in alcoholic solution), merely induces the formation of the hydroxyethylated bromide, and, in the absence of water, apparently gives rise to vinyltriethylphosphonium bromide; its behaviour in this respect is analogous to that

of trimethylamine, which slowly combines with ethylene bromide, forming the compound $N(CH_3)_3(BrC_2H_4)Br$; when subjected to the further action of trimethylamine, this latter is deprived of hydrogen bromide. Again, whereas triethylarsine and the bromethylated bromide readily combine, forming the phospharsonium bromide, triethylstibine affords no similar compound; the latter also behaves irregularly with ethylene bromide, which readily acts on triethylarsine. Hofmann also refers to a peculiar behaviour of bromethyl-trimethylphosphonium bromide with triethylphosphine, but without describing it. One other interesting observation should be mentioned, namely, that whereas ethylene chloride, like the bromide, readily combines with triethylphosphine, ethylene iodide is merely deprived of hydrogen iodide by the phosphine.

In a later paper (May, 1861) attention is drawn to the interesting difference in behaviour of the methylene and ethylene compounds. Methylene chloride—and also the iodide—forms first a chloromethyl-triethylphosphonium chloride, a beautifully crystallised substance, which then fixes a second molecule of the phosphine. But the methylenehexethyldiphosphonium chloride produced in the latter case cannot be brought into contact with water without undergoing immediate decomposition, thus



a change taking place which, in the ethylene series, occurs only when the base is subjected to a high temperature.

Hofmann speaks of methylene dibromide behaving differently, but does not state in what way. The somewhat similar behaviour of iodoform (as well as of chloroform and bromoform) was described by him at an earlier date (October, 1859). The interaction of iodoform and triethylphosphine is of a most vigorous character; the product, which may be recrystallised from alcohol, is a triphosphonium triiodide, from which other salts can be readily prepared. The corresponding hydrate cannot be obtained, however, as reduction takes place on digesting the iodide with silver oxide, a mixture of *methyltriethylphosphonium* hydrate with triethylphosphine oxide being formed.

Carbon tetrachloride, in like manner, combines with 4 molecular proportions of the phosphine, forming a tetraphosphonium compound; but the product cannot be isolated owing to its extraordinarily deliquescent nature and the impossibility of touching it with a solvent without decomposing it; water converts it into the compound obtained from chloroform, triethylphosphine oxide and hydrogen chloride.

It is manifest that in all these cases the tendency of triethylphos-

phine to combine with oxygen (and sulphur) which distinguishes it so sharply from triethylamine, enables it to act in presence of water (or sulphuretted hydrogen) as a powerful reducing agent.

Hofmann's last communication with reference to triethylphosphine was made to the Royal Society in December, 1861; in it he describes its behaviour—as well as that of triethylamine—with chloracetic ether, which is shown to be precisely similar to that towards the alcoholic haloids previously studied. Attention is specially directed to the change that the hydrate formed from the chloride at once undergoes, losing alcohol and forming a glyocol derivative.

A long interval elapsed after the publication of Hofmann's papers on tertiary phosphines and of the phosphonium compounds derived from them, although, as he has himself remarked, the study of the primary and secondary phosphines, the examination of which promised even more noteworthy results than that of the bodies before investigated, still remained to be achieved. It is clear that the peculiar tenacity of purpose which was one of his most striking characteristics led him to bear this problem constantly in mind, for in his "New Researches on the Phosphorus Bases," communicated to the Royal Society in March 1872 (*Proc.*, **20**, 221—239), after referring to the lapse of 12 years, he states that—

"New tasks of life have since that time presented themselves, and I have not been able to devote myself as much to research as in former days. Nevertheless, numerous attempts were made to procure the primary and secondary phosphines, which were clearly indicated by theory and partly even by M. Thénard's early observations. For a long time, however, these experiments proved unsuccessful, and it was only in the course of last summer that I at last discovered an easy method for their production."

And the manner in which the new method was discovered is stated in the following interesting passage—

"The starting point of the new series of researches was a lecture experiment. Wishing to exhibit to my class the decomposition of phosphoretted hydrogen by the spark current of an induction coil, I was unable to procure by any of the methods hitherto described, phosphoretted hydrogen of sufficient purity for this experiment. I was thus led to select a rather unusual substance as a source for phosphoretted hydrogen, namely, the beautiful compound of the latter with hydriodic acid, generally designated as phosphonium iodide. If a slow stream of water, or better, of potash or soda, be allowed, by means of a dropping tube, to flow into a small vessel containing phosphonium iodide, a regular current of perfectly pure phosphoretted hydrogen is evolved. . . . The facility with which phosphonium iodide is thus seen to split up into its constituents . . . led me to think that this body might be made available for the preparation of the compounds I had so long endeavoured to obtain. Two different processes suggested themselves, both aiming at a reproduction of the conditions under which, as

I have shown now more than 20 years ago, the alcohol derivatives of ammonia are readily obtained. For this purpose it was necessary to disengage phosphoretted hydrogen in the presence of an alcohol iodide under pressure. This could be easily accomplished by submitting a mixture of an alcohol iodide and phosphonium iodide in sealed vessels to the action of an agent . . . slowly liberating the phosphoretted hydrogen from the iodide."

This anticipation was not only fulfilled, but the remarkable observation was made that on heating phosphonium iodide along with zinc oxide and an alcoholic iodide the primary and secondary phosphine were exclusively produced, although on submitting the iodide to the action of an alcohol only the tertiary phosphine and a quaternary phosphonium iodide were formed. The separation of the primary and secondary phosphine also proved to be a simple task, the salts of the former being easily decomposed by water, whilst those of the latter are stable in presence of water but immediately decomposed on adding an alkali. Besides the two methyl- and the two ethyl-phosphines, Hofmann describes in this paper the two benzylphosphines obtained by means of benzyl chloride. He subsequently described the primary and secondary isopropyl, isobutyl and isoamyl phosphines.

Benzylphosphine, like the two methyl and the two ethyl compounds, exhibits basic properties, and, like them, is at once oxidised on exposure to air, but dibenzylphosphine does not dissolve in acids, and oxygen is without action on it, even at an elevated temperature. On oxidation with nitric acid, the methyl- and ethyl-phosphines yield phosphinic acids, the primary base giving a dibasic acid, *e.g.*, $\text{CH}_3\cdot\text{PO}(\text{OH})_2$, and the secondary base a monobasic acid, *e.g.*, $(\text{C}_2\text{H}_5)_2\text{PO}(\text{OH})$. Dimethyl- and the two ethyl-phosphines unite with sulphur and carbon bisulphide, but far less energetically than triethylphosphine,* as the compound of dimethylphosphine with carbon bisulphide is not crystalline, it is easy to demonstrate the absence of trimethylphosphine among the products of the interaction of phosphonium and methyl iodides.

The higher homologues of ethyl- and diethyl-phosphine closely resemble these compounds, but, as is usually the case, become less well characterised as the series is ascended. In his later papers on the subject, Hofmann describes a number of mixed phosphines and phosphonium derivatives, such, for example, as ethylisopropylisobutylphosphine and the methiodide formed from this; these were obtained by methods similar to those used in preparing corresponding

* The action of sulphur on the primary and secondary phosphines was described by Hofmann and Mahla in a paper published after his death—the last to appear in the *Berichte* bearing his name (1892, 2436). They give rise to thiophosphinic acids, such as $\text{PSEt}_2\cdot\text{SH}$.

nitrogen compounds, by subjecting a primary phosphine to the action of an alcoholic iodide and repeating the treatment with the secondary phosphine so produced.

Attempts to prepare polyphosphines from phosphonium iodide and ethylene bromide and chloroform were unsuccessful, owing to the reducing action exerted by the hydrogen iodide, ethylene bromide giving rise to ethylphosphine and chloroform to methylphosphine.

Hofmann, however, foresaw that such compounds would be eventually produced in other ways, and, at the close of his paper, points out that a solution of phosphine in ether acts readily on iodoform, but he does not appear to have afterwards completed this investigation.

The acids obtained by oxidising the primary and secondary phosphines were shown to be readily converted into corresponding di- and mono-chlorides by means of phosphorus pentachloride, the chlorides, in the case of the methyl compounds, being well crystallised substances, which water at once decomposes.*

Although in the interval since his researches were published our knowledge of the phosphines and allied compounds has been considerably increased, chiefly owing to the discovery of phenyl derivatives by Michaelis and his pupils, in the case of this group, as in that of the amines and substituted ammonium compounds, we owe all that is fundamental to Hofmann—the properties which he has shown to be characteristic of the primary, secondary and tertiary ethyl derivatives of phosphine being characteristic of all other similarly constituted compounds.

This is true, for example, of the phenyl- and of the phenyldiethyl- and phenyldimethyl-phosphine prepared by Michaelis (*Annalen*, 1876, 181, 265), and, in many respects, even of the triphenylphosphine discovered by Michaelis and v. Soden (*ibid.*, 229, 295). Although the latter compound, as was perhaps to be expected, is odourless, and does not combine directly with oxygen or with carbon bisulphide, it yet readily combines with sulphur, with alcoholic iodides and with chlorine, and its chloride, Ph_3PCl_2 , is converted into the corresponding oxide by the action of water.

In view of these facts, it is noteworthy that triphenylstibine is incapable of combining with alcoholic iodides; that its chloride is stable in presence of water; that the hydroxide prepared by the action of alcoholic potash on the chloride, which melts at 212° , shows no tendency to lose water and form a corresponding oxide;

* Attention may be here drawn to the fact that an account of experiments with phosphonitrichloride was published by Hofmann in 1884 (*Ber.*, 17, 1909).

and that this hydroxide is readily reduced by sulphuretted hydrogen, being converted into the stibine, which apparently does not combine with sulphur.

* * * * *

After the publication of his memoir on the substituted ammonium compounds in 1851, until the commencement of his work with Cahours on the phosphorus bases in 1855, no important subject seems to have engaged Hofmann's attention, and it was not until 1858 that he began to turn his attention to the polyammonias, the first of his "Notes of Researches on the Polyammonias"—of which 24 in all were published in the *Proc. Roy. Soc.* (1858—1863)—bearing the date February 4, 1858 (*Proc.*, 9, 150). Unfortunately, no collected account of his investigations in this field was ever published.

It is clear that the fact that the greater number of natural alkaloids contain several atoms of nitrogen, led him to study such compounds. Having referred to this in the paper in question, he states:—

"It was long my intention to extend my researches to the polyammonium bases. But my attention has been specially called to the subject of the beautiful results obtained of late, especially in France, by the study of the polyacid alcohols, by the experiments of M. Berthelot, and more particularly by the classical researches of M. Wurtz, which enable us to take a general view of this subject."

Having pointed out how a series of bases derived from two molecules of ammonia, bearing to each other the relations observed in the case of the monamines, might arise from the introduction of a dyad radicle, he calls attention to experiments made about five years before by Cloez on the action of ethylene bromide on ammonia, which appeared to show that three bases, viz., "Formylia," C_2H_3N , "Acetylia," C_4H_5N , "Propylia," C_6H_7N , were formed.

Hofmann, however, points out that it appeared probable, judging from their physical properties, that these were the diammonium compounds of which he was in search, namely, mon-, di- and tri-ethylenediamine, and he quotes evidence proving that the acetylia of Cloez in reality had the composition of ethylenediamine. Of course, he at once proceeds to generalise, and refers to experiments made with the object of preparing triamines.

The second note (*Proc. Roy. Soc.*, April 15, 1858) briefly describes the results obtained with aniline and chloroform, by the interaction of which the *monacid* diamine, $[CH(NPh)NPhH]$, diphenylformyl-diamine, was obtained.

The next note relates to a different subject, but in the fourth (May, 1858) an account is given of the action of ethylene bromide on aniline. The product is spoken of as ethylenephénylamine, $(C_2H_4)NC_6H_5$, although the probability that it was diethylenediphenyldiamine is

clearly recognised. In a later note (the sixth) this is shown to be the case, and an intermediate compound, ethylenediphenyldiamine, is described, together with the two corresponding compounds formed from ethylamine and ethylene bromide.

Hofmann's chief reason for assuming that a diamine was formed was the observation that the product combined with methyl iodide in the proportion $\text{CH}_3\text{I} : 2\text{C}_2\text{H}_4\text{NC}_6\text{H}_5$. The importance of this argument was dwelt on at a later stage in the inquiry (May, 1861) in the 14th note, in which the diagnosis of diamines is discussed. It is there pointed out that the residual hydrogen in each of the linked ammonia molecules is invariably affected in the same manner, the substitution of ethyl being never limited to one equivalent of hydrogen. When, however, the ammonia is converted into an ammonium compound by the action of ethyl iodide, the true nature of the substance is revealed; a monamine gives rise to only one compound, a diamine to two—tetrethylethylenediamine, for example, yielding both a pentethylated hydriodide and a hexethylated diiodide. The value of the method in cases in which easily decomposable compounds are dealt with is insisted on.

The seventh note on polyammonias (December, 1859) is in a measure controversial,* for in it Hofmann sustains the conclusions he had previously arrived at as to the nature of the action between ammonia and ethylene bromide against Cloez, who had rejected the formulæ he had assigned to the diatomic derivatives of phenylamine and ethylamine and had continued to assert that the products were monamines. After criticising his adversary's arguments, he passes to his facts and shows that the gaseous density of ethylenediamine as determined by him was that of a mixture of the anhydrous base and water formed by the decomposition of the hydrated base, and consequently that Cloez had been misled in placing reliance on the number he had obtained. He then proceeds to prove that the density of the anhydrous base was in accord with the formula he had assigned to it, whereby it was represented as a diatomic ammonia.† He shows also in this note that the compound named *acetenamine* by Cloez was diethylenediamine. As on subjecting the two bases to the action of ethyl iodide, in the one case the products were two volatile and one fixed base, and in the other one of each kind, there could be no

* In his obituary notice of Griess, who helped him in this inquiry, Hofmann observes that—"Few who now use ethylenediamine and diethylenediamine remember that it required a long controversy with Cloez to secure for these compounds the recognition of the position in the system of organic chemistry which they now occupy."

† A further account of observations in explanation of the "anomalous" vapour density of the hydrated base is to be found in the ninth note.

doubt as to the accuracy of the conclusions arrived at—and the manner in which he sums up his case, towards the close of the note, shows that he is convinced of this—

“In the present state of science we rely upon a certain number of considerations which guide us in the construction of a chemical formula. These are—the study of the origin of a body; analysis; observation of the physical properties, and, especially of the boiling point; the determination of the vapour density; and lastly, the examination of its metamorphoses. I have endeavoured to look at the question under discussion from these several points of view; experiment has invariably given the same reply.”

A more concise statement of procedure could not be made.

The conclusion is pointedly stated in this note that “it follows from this controversy that the diatomic alcohols imitate the monatomic in their deportment with ammonia;” in other words, that a series of bases exist related to glycol in the same way that the three ethylamines are related to ethyl alcohol.

Meanwhile, the attempt was being made to associate a still larger number of ammonia molecules. Thus, in the fifth note (June, 1858), we find a description of the action of carbon tetrachloride on aniline, which is shown to give rise to the triamine, $C_{19}H_{17}N_3 = C(NPh)(NPhH)_2$, now known as triphenylguanidine.

In discussing the relations between the monatomic and polyatomic bases towards the close of his researches on the phosphorus bases (*Proc. Roy. Soc.*, **10**, 619), Hofmann fully considers the many ways in which diatomic bromides may act on bases to form polyatomic bases of a higher order; and the following eminently characteristic sentence occurs at the close of the paper—

“I have but a faint hope that I may be able to trace these new paths in the numerous directions which open in a variety at once tempting and perplexing. Inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium and tetrammonium compounds begin to unfold themselves in unexpected variety. One of the most remarkable compounds belonging to the triammonium group is *diethylenetriamine* . . . This base, the *first triacid triammonia*, forms splendid salts”

The description of the base was given about a year later in the 16th note on polyammonias, but only in the briefest terms. It is present, together with triethylenetriamine, in the portion boiling at $200-220^\circ$ of the mixture of bases obtained on heating ethylene bromide with ammonia. They form a great variety of salts, most of which crystallise with facility; their separation was chiefly effected in the form of chlorides, bromides and iodides, or of platinum salts and gold salts. Both are described as powerfully alkaline liquids, soluble in

every proportion in water and alcohol, but which do not exhibit the tendency to form definite hydrates so pronounced in the diamines.*

A subsequent note (the 17th) contains an account of the di- and tri-ethylenetriethyltriamines obtained from ethylamine and ethylene bromide; these closely resemble the ethylenetriamines, exhibiting the same tendency to form diatomic salts.

A still higher stage is reached in the next note (the 18th), which is devoted to tetrammonium compounds, several of which formed from ammonia, ethylamine and diethylamine respectively and ethylene bromide are described; the octethylated tetrammonium compounds derived from diethylamine are remarkable for their definite characters, being still crystalline.† But it must be confessed that, except as affording proof that a series of polyammonias can be produced corresponding with the polyethylenic glycols obtained by Wurtz, the various substances described offer few points of novelty or interest. Indeed, the following words used by Hofmann, in the course of the note under consideration—

“As a chemical theory expands and becomes more and more consolidated, the interest attached to the individual compounds used as scaffolding in raising the structure become less and less, diminishing in fact in the inverse ratio of the number of compounds which the theory suggests,”

may not inappropriately be applied to the separate results of his inquiry into the polyammonias; and the fact that they were never published in a collected form is perhaps ascribable to his having recognised that in such a case it was unnecessary to put details on record.

Ethylenediamine was prepared on a large scale by Hofmann in 1872 with the aid of ethylene chloride formed in the manufacture of chloral, and its properties were more fully studied, especially with the object of contrasting its behaviour with that of the primary monamines (*Proc. Roy. Soc.*, **20**, 425).

His attention being thus re-directed to the diamines, he was led also at this time to prepare propylenediamine (*Ber.*, 1873, 308). This was found to boil only 3° higher than ethylenediamine, and, like the latter, to attract moisture with most remarkable avidity.

* The formation of these hydrates again occupied Hofmann's attention in 1873. In a note on propylenediamine (*Ber.*, **6**, 311), after referring to the fact that ethylenediamine which has been dried by prolonged digestion with caustic potash still retains a molecular proportion of water (he had described it in 1860 as forming a beautiful crystalline, very stable hydrate—*Proc. Roy. Soc.*, **10**, 597), he points out that when the propylene compound is similarly treated, two molecular proportions retain only one molecular proportion of water.

† The production of what appears to be even higher terms, yielding amorphous salts, was referred to by Hofmann in 1870 (*Ber.*, **3**, 762).

It is clear that the subject continued to interest him, as he published a number of communications, as late as 1890, describing the various amines prepared with the aid of ethylene chloride, especially diethylenediamine, diethylenetriamine and triethylenetetramine; having obtained diethylenediamine—now recognised as a cycloid—in the crystalline state, he was led to identify it with the commercial product first sold as spermin and afterwards as piperazine (*Ber.*, 1890, 3297, 3711, 3723).

All the researches on the polyammonias to which reference has thus far been made concern ethylene derivatives. That Hofmann, however, "had repeatedly endeavoured to produce the diatomic bases corresponding to the aromatic amines" we can well believe. As he points out in his 19th note (December, 1861), the method for producing such compounds appeared obvious, the idea naturally presenting itself to look to dinitrobenzene as the source from which phenylenediamine might be obtained; in fact, it seemed very probable that the nitrophenylamine which Muspratt and he had prepared was but the first product of reduction, and that prolonged treatment would lead to the complete reduction of the dinitro-compound. All such attempts were unsuccessful, however.

Hofmann's attention, he tells us, was drawn again to the study of the aromatic diamines under peculiar circumstances—by his receiving a specimen of a crystallised base, obtained as a secondary product in the aniline works of M. Ch. Collin, of Paris. This proved to have the composition of tolylenediamine, and obviously owed its origin to the presence of toluene in the commercial benzene used in preparing aniline. Finding that dinitrotoluene was easily reduced by means of iron and acetic acid—

"The method of reduction now generally adopted in the manufacture of aniline—the behaviour of the dinitro-compounds of the homologues of toluene, especially dinitrobenzene, was at once examined—with the result that phenylene diamine (meta) was discovered."

The closing words of this note, in which Hofmann refers to MM. Collin and Coblentz (the chemical director of the works) for the materials placed at his disposal, are not only strikingly characteristic of his style, but also expressive of an important truth which is not always sufficiently recognised—

"By facilitating the scientific elaboration of the new diatomic compounds, these gentlemen have endeavoured most gracefully to acknowledge the debt of gratitude which the aniline industry owes to theoretical inquiries in organic chemistry."

Equally graceful is the manner in which, on another occasion, he

returns his thanks for the beautifully crystallised cyanine placed at his disposal by M. Menier—

“Though proud of her office as guide of industry, science acknowledges without blushing that there are territories on which she cannot advance without leaning on the strong arm of her powerful companion. Joint labours of this kind cannot fail to seal the pledge of alliance between industry and science.”

But little more remains to be said of his researches on the poly-ammonias. Two of the notes refer to the discovery of new bases among the secondary products of the manufacture of aniline, viz., paraniline, $C_{12}H_{14}N_2$, and martylamine or xenylamine, since recognised as paramidodiphenyl. One relates to the discovery of hydrazobenzene as an intermediate product in the formation of benzidine from azobenzene; and another to the production of (para)phenylenediamine from the nitraniline obtained by nitrating acetanilide, this being the last of the notes on poly-ammonias.

But it must not be forgotten that the colouring matters produced from aniline were recognised by Hofmann as poly-ammonias, and probably the most important of all his notes on such compounds is the 20th (*Proc. Roy. Soc.*, Feb., 1862, **12**, 2), in which he gives the results of his analyses of rosaniline and its salts. The name rosaniline was felicitously chosen by him

“To commemorate the origin of the compound in its name, since it appeared to be the prototype of a number of similar substances obtainable by similar processes from the homologues, and probably also from the analogues, of aniline.”

Nicholson, who first obtained the base and its salts in the state of purity, had termed it roseine.

Beyond defining rosaniline as a triacid triamine, Hofmann was unable to offer any opinion regarding its constitution; but it is clear that he foresaw that such compounds were of a different order from those he had previously studied. In fact, a few months later, when discussing the nature of cyanine, he remarks that—

“The theory which (in 1852) satisfactorily represented the constitution of the nitrogen bases then examined, requires an expansion to include the tinctorial ammonias added to our knowledge during the last decade. The time for the enunciation of this amplified theory has not yet arrived.”

Nor did it fully arrive until many years later—not until 1876—when Emil and Otto Fischer began the publication of the remarkable series of observations which led them to discover the relation of rosaniline and its congeners to the hydrocarbon triphenylmethane—a research of the utmost importance in relation to both theory and

practice. But in the interval, a very large amount of valuable work had been done by Hofmann as well as by others which all contributed to the solution of the problem. It should especially be mentioned, that the study of the behaviour of rosaniline with nitrous acid, to which Hofmann first drew attention in 1862, practically gave the clue to its composition.

* * * * *

The attempt has been made in the course of the foregoing account to broadly trace the gradual development of Hofmann's researches on amines and ammonium compounds and the allied phosphorus derivatives, the record of which necessarily forms the chief chapter in a history of his scientific labours. At the time of his departure from England, he had practically completed his studies of this class of compounds; indeed, with the notable exception of the research on primary and secondary phosphines, almost all of his contributions to our knowledge of the chemistry of aminoids—including those on colouring matters, of which Dr. Perkin has given so interesting an account—were the outcome of work done during a period of less than 20 years in the modest quarters and with the modest appliances afforded by the Royal College of Chemistry in Oxford Street, the exterior of which is shown in the figure opposite.

The building had a frontage of only 34 ft., its depth being 53 ft. The whole of the first floor was occupied by the students' laboratory, the bench at which the seniors worked being in front of the upper row of windows seen in the figure. On the ground floor, the space on the right of the hall passage was devoted to the Professor's use as a private laboratory, his private room being on the left at the back of the building; the room in front was the balance room and library. The basement was used for larger and rough operations, and contained furnaces, a steam boiler, &c. The lecture theatre was built out at the back. The porter kept apparatus for the use of students, chemicals, &c., in the cellars under the street pavement.

But the record of his activity as an English Professor would be altogether incomplete, and the extent of his services to chemical science would not be sufficiently indicated, if some reference were not made to other work emanating from the Oxford Street laboratory.

Hofmann, as Dr. Perkin reminds us, was practically the discoverer of benzene in coal tar. We must go back fully 50 years to find the record of the discovery in a modest note in *Liebig's Annalen* (September, 1845, 55, 200), "Ueber eine sichere Reaction auf Benzol; von Dr. Aug. Wilh. Hofmann, Privatdocenten der Chemie an der Universität, Bonn."

The reaction described consists in converting the benzene into nitro-



benzene, then reducing by means of acid and zinc,* and testing for the aniline with bleaching solution. It is shown that a single drop suffices for the test, and that in this way it is possible to detect the presence of benzene in a variety of products.

Events, as we know, have proved the discovery to be one of enormous practical importance; the following passage, in which it is recorded, is therefore of interest—

“Man findet vielfach in Abhandlungen und Lehrbüchern angegeben, dass das Steinkohlentheeröl Benzol enthalte, allein es ist mir keine Untersuchung bekannt geworden welche sich direkt mit dieser Frage beschäftigt hätte. Von meinen Versuchen über die organischen Basen des Steinkohlentheeröls her, besass ich noch eine Quantität der leichten Kohlenwasserstoffe welche bei der Rectification des rohen Destillationsproduktes des Steinkohlentheers zuerst übergegangen waren. In diesem Oele musste das Benzol enthalten seyn, wenn sich bei der Destillation der Steinkohle überhaupt welches bildet. Ich unterwarf diese Flüssigkeit zu dem Ende einer neuen Destillation; sie gerieth bei 105° ins Sieden, der Siedepunkt stieg aber fortwährend noch höher. Ich sammelte was bis 118° überging und rectificirte das Destillat von Neuem; es begann jetzt schon bei 94° zu sieden und der Siedepunkt stieg weit langsamer als zuvor. Was bis zu 105° überdestillirte wurde dem Versuch unterworfen; es liess sich mit Leichtigkeit erkennen, dass diese Flüssigkeit eine grosse Quantität *Benzol* enthielt.”

Hofmann was not the man to leave such an observation unexploited, especially when the necessity of obtaining aniline for his researches pressed upon him, and although he did not personally undertake the investigation, it was in the Oxford Street laboratory that Mansfield, a few years afterwards, carried out his memorable “Researches on Coal Tar” (*Chem. Soc. J.*, 1849, **1**, 446), which were attended with so tragic an end—researches which, he tells us, were commenced at the request of Hofmann and conducted under his advice. The investigation appears to have been the first in which the separation of a constituent of a mixture of liquids by fractional distillation was promoted by using a still head kept at a temperature below the boiling point of the less volatile constituents.

Mansfield not only separated benzene from coal tar, but showed how it might be readily prepared on a large scale of any desired degree of purity, of course availing himself of Faraday’s previous

* Hofmann appears to have been the first to use a metal together with an acid as a reducing agent, and to recognise the value of “nascent” hydrogen as a means of reducing nitro-compounds. Bechamp’s discovery of the use of ferrous salts as reducing agents was not communicated to the French Academy until July 1854, and the use of iron and an acid was described soon afterwards by him in the *Annales de Chimie*. Such being the case, it is remarkable that the discovery of aromatic diamines was not more easily made by him, and that instead of attempting to reduce dinitrobenzene by means of sulphuretted hydrogen only, he did not at once try other reducing agents.

observations. He at the same time pointed out that it might be procured to any extent from coal tar, or from the light naphtha, in which, he said, it had hitherto been "wasting its sweetness on the desert air;" and that the promises which it made of utility were sufficiently numerous to encourage a belief that it might form a special object of manufacture and of commerce.

But the study of his paper promotes mixed feelings. In the introductory portion, in which an account is given of previous investigations of products of destructive distillation, after referring to the dearth of knowledge of coal tar products, he remarks—

"It appears somewhat strange that, in this country, where coal tar is so exceedingly plentiful, our chemists should have been contented with the discovery of naphthalene, and should have allowed others less fortunate than ourselves in being able to command abundance of this almost national production, to inform us of the existence at our feet of vast quantities of aniline, of paranaphthalene, and of other remarkable substances; and it appears, perhaps, no less singular that we should have failed as yet in applying them, when discovered, to the practical uses which they will, no doubt, some day claim."

It is in the highest degree remarkable that an aniline colour industry so soon afterwards came into existence and acquired such importance here; that an industry of corresponding magnitude was in consequence founded on Mansfield's researches; that an anthracene industry subsequently arose; and, lastly, that the azo-colour industry, although conceived, we must allow, in the Marburg laboratory, yet passed through its whole period of gestation—first in the College of Chemistry and then in an English brewery—and sprang into being in this country. The record is a glorious one. For a time, at least, we were not open to the reproach conveyed in Mansfield's words, especially during Hofmann's presence among us. But how different is the condition of affairs now. It is fast becoming necessary to go back to the dim records of the past for an account of English victories in such fields; the men who gained them are all but gone, without leaving successors worthy of the name. Hofmann, Griess, Simpson, Maule and Nicholson have no modern English equivalents; but the type has not merely been preserved but multiplied and even improved abroad. Perkin alone we rejoice to retain among us, and still more that he has retired into a higher sphere of usefulness.

Yet coal tar may still be characterised in Mansfield's words as a national production, and it is an appalling fact, that after having successfully established such industries, we should have allowed them largely to slip through our fingers, in consequence of the failure of our industrial chiefs to march with the times. Nor must we forget that Hofman himself warned us at the very outset, when—foreseeing,

it would seem, what would be the course of events—he insisted upon the importance of cultivating natural science in its bearings upon the whole mechanism of society, as the mainspring both of industry and national prosperity, and, in Humboldt's words, pointed out the fate in store for those who neglected to fully apply science to manufactures.

And it is more than strange, not merely "somewhat strange," that we should have contributed so little, since Mansfield's time, to the knowledge of the chemistry of coal tar, a branch of our subject which has been cultivated with the utmost zeal and success elsewhere.

Mansfield clearly established the existence of toluene, as well as of benzene, in coal tar; he also separated a fraction boiling at about 140—145°, which he suggested might prove to contain cumene identical with that from cuminic acid; and another fraction, boiling at 170—175°, which it was thought might be cymene. It is in no way surprising that he should have failed in obtaining more definite results. From the experience since gained we know that it is impossible to separate any other single substance besides benzene and toluene from coal tar naphtha by mere distillation, owing to the presence in it of a variety of isomeric benzenes of nearly the same boiling point, as well as of paraffinoids and unsaturated hydrocarbons of several series. It was not, in fact, until Fittig and Tollens devised synthetic methods of preparing the benzenes, similar to those used long before by Frankland and by Wurtz, that their properties became sufficiently known to permit of their recognition in the naphtha; and another long interval elapsed before the isolation of the separate modifications was successfully accomplished by Jacobsen through the agency of sulphonic acids.

Even the relation of toluene to benzene was not established until 1864, when Fittig and Tollens prepared the hydrocarbon from bromobenzene, methyl iodide and sodium (*Liebig's Annalen*, **131**, 303); Fittig and Tollens, in fact, engaged in their research in the expectation of obtaining hydrocarbons which *might perhaps* prove to be identical with the homologues of benzene. Kekulé's luminous exposition of the nature of benzene—the bright spot around which all other discoveries relating to benzenoid compounds, the characteristic and essential constituents of coal tar, must ever centre—was not published until 1865.

We now know that the naphtha contains besides benzene and toluene—not to mention thiophene, the very shadow of benzene, as Victor Meyer has shown in the course of his classical researches—the three dimethylbenzenes and ethylbenzene, of which the last, however, has not yet been actually isolated, 1 : 2 : 4- and 1 : 3 : 5-trimethylbenzene, and 1 : 2 : 4 : 6-tetramethylbenzene. Numerous solid

polycycloid hydrocarbons have been separated from higher fractions of the tar. Whilst some few of the products in tar are formed by the breaking down of benzenoid compounds present in coal, there is little doubt that the majority of its constituents are products of synthetic changes occurring at high temperatures, but our knowledge on these subjects is very vague at present.

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Before passing from the hydrocarbons it should be pointed out that we owe a not inconsiderable part of our knowledge of one of the homologues of benzene, viz., 1 : 3 : 5-trimethylbenzene or mesitylene, to Hofmann, who examined it long before its existence in coal tar was recognised; in fact, this only dates from 1869, when Fittig and Wackenroder showed that coal tar cumene was a mixture of the two trimethylbenzenes we now know to be the 1 : 3 : 5- and 1 : 3 : 4-modifications. Sir R. Kane, who first obtained mesitylene by distilling acetone with sulphuric acid, had represented it by the formula C_6H_4 , which at a later date was doubled by chemists on evidence afforded by vapour-density determination made by Cahours. Hofmann (*Chem. Soc. J.*, 1849, 2, 104) drew attention to the fact that the boiling point of mesitolole (as he terms it—no doubt, in order to harmonise its name with that of benzole) was much higher than that a hydrocarbon $C_{12}H_8$, containing the same number of carbon atoms as benzene, would be likely to possess, and inferred that the true formula was $C_{18}H_{12}$ (C_6H_{12} in our present notation), from the fact that when subjected to the action of moderately concentrated nitric acid the hydrocarbon gave a nitro-derivative (dinitromesitylene) convertible by reduction into a nitromesidine the formula of which could only be deduced from that of a hydrocarbon of the formula $C_{18}H_{12}$. Tribromomesitylene and mesitylenesulphonic were obtained for the first time in the course of this work.

This communication affords another illustration of the uncertain state of belief in which chemists were then plunged regarding vapour densities, and serves to emphasise the value of Canizzaro's services in this connection, for, referring to Cahours's determination of the vapour density of the hydrocarbon, Hofmann remarks—

“ If this determination be correct, one equivalent of mesitolole would represent not less than 6 volumes of vapour, a number which has never been observed in any similar case. All the well investigated hydrocarbons have given hitherto 4 volumes. It is possible that the specific gravity of the mesitole vapour is subject to similar variations as have been observed with acetic, butyric, valerianic acids, and several other compounds; it is possible, likewise, that an equivalent of mesitole is actually represented by 6 volumes of vapour, and this anomalous condensation may assist in explaining the difference between the constitution of this body and cumole, which, like the other hydrocarbons, contains only 4 volumes of vapour. Be this, however,

as it may, the subject requires further investigation. I have hitherto been prevented repeating the determination of the specific gravity from not having obtained the hydrocarbon of a perfectly constant boiling point."

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Among the services rendered by Hofmann there is one which should be referred to before passing to other subjects, as it has been of immense value not only in the laboratory but especially in working on the large scale, simple though it be, viz., that recorded in the following passage in the paper on the preparation of nitraniline by Muspratt and Hofmann communicated to the Society in March 1846 (*Chem. Soc. Memoirs*, **3**, 119)—

"For our research we had to prepare a large quantity of dinitrobenzol. The transformation of nitrobenzol into dinitrobenzol proceeds very slowly, even when it is boiled repeatedly with the strongest nitric acid. It is obtained, however, very speedily by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid, and concentrated sulphuric acid, as long as the liquid remains homogeneous."

The use of sulphuric acid in nitrating benzene, it is well known, is of the first importance as enabling the operation to be effected in an economical manner; and in many cases nitration is only possible in its presence, owing to the occurrence of oxidation when nitric acid is used alone: the manufacture of gun-cotton and of nitroglycerin are cases in point. There is good reason to suppose that the sulphuric acid has a definite determinative effect on the course of the change, and that it does not merely serve to maintain the strength of the nitric acid (compare *Chem. Soc. Proc.*, 1891, 89).

Another important practical step taken by Hofmann consisted in using acetanilide for the preparation of derivatives of aniline. For an account of this reference must be made to a paper by Mills, then one of his students (*Proc. Roy. Soc.*, 1860, **10**, 589), describing the preparation of brom- and chlor-aniline. Hofmann explains, in a footnote, how Arppe's observation that tartronitrophenylamide, when hydrolysed, gave a nitraniline (para-) isomeric with that obtained from dinitrobenzene had led him to "nitronate a more easily procurable phenyl compound, viz., acetylphenylamide," the result being that he found it could be used with considerable advantage. On this occasion he took the opportunity of pointing out that the dinitromel-aniline he had prepared 10 years previously also gave the nitraniline isomeric with that from dinitrobenzene when hydrolysed.

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There is abundant evidence that Hofmann at all times took the keenest interest in current problems unconnected with his own special researches, displaying great judgment in their discussion. Thus in a brief postscript to a paper by Field on the formation of cumonitrile

(*Liebig's Annalen*, 1847, **65**, 56), he refers to experiments on the preparation of butyronitrile and valeronitrile which he had been induced to make in consequence of the observations of Frankland and Kolbe on the intimate connection of the nitriles with the cyanides of the organic radicles, a discovery which we know excited the greatest interest at the time.

A later communication (*Chem. Soc. J.*, 1850, **3**, 121) entitled a "Note upon the Action of Heat upon Valeric acid, with some Remarks upon the Formulæ of the Alcohol Radicles"* is devoted to the discussion of the views of these same chemists on the molecular composition of the alcohol radicles, and deals, therefore, with one of the most important fundamental questions of chemical theory. The hydrocarbons obtained by Frankland from the alcoholic iodides by the action of zinc and described under the names methyl, ethyl and amyl, were, as all know, at first regarded as the actual radicles; but, as Hofmann tells us, Laurent and Gerhardt pointed out in a report to the French Academy on Frankland's work that they might with more probability be considered as homologues of marsh gas. He very fully discusses the two points of view, and with great acuteness strongly advocates the latter; the concluding paragraph of the paper may be quoted as an illustration of the foresight he displayed—

"Should experiment, however, prove that the so-called alcohol radicles are actually the homologues of marsh gas, as supposed by Messrs. Laurent and Gerhardt, these substances, although losing the prestige of radicles in the conception of the electrochemical theory, would certainly not present less interest. Chemists know the remarkable manner in which the researches of Dumas, Regnault, and Melsens have linked the methyl series to marsh gas, and the facility with which we pass from marsh gas over to chloride of methyl. We have a right to expect that the higher homologues of marsh gas will exhibit a similar deportment. If this be actually the case, the action of chlorine upon ethyl would place the whole series of the butylic alcohol at our disposal; in fact, we should have discovered a general method of forming the homologues of common alcohol, and this series, presenting as yet so many gaps, would ere long be as complete as the parallel group of the fatty acids."

It was in the hope of passing from the nitriles to the alcohols, doubtless with the object of completing the series, that Buckton and Hofmann were led to subject the nitriles to the action of sulphuric acid (*Phil. Trans.*, 1856, 453—480). They anticipated that the interaction would resemble that of hydrogen cyanide and sulphuric

* This follows an account by Captain Reynolds on the preparation of propylene by passing amyl alcohol through a red-hot tube. It is of interest, historically, that Reynolds speaks of the name propylene as being, "like the rest of the series, derived from the corresponding alcohol, in this case still unknown, and for which the appellation of propylic alcohol has been suggested by Dr. Hofmann."

acid; that acetonitrile, for example, would yield carbonic oxide and the acid sulphate of methylamine, just as carbonic oxide and the acid sulphate of ammonia are formed from hydrogen cyanide; instead, however, of such products, they obtained the sulphonic acid of the acid corresponding to the nitrile, and disulphonic acids formed by the displacement of the carboxyl group when the action of the acid was prolonged.

These results led Hofmann to instigate experiments on the action of sulphuric acid on anisic and salicylic acids; those with the former acid were carried out by Zervas, who obtained sulphanisic and anisol-disulphonic acids, whilst Duppa prepared similar derivatives from salicylic acid (*Chem. Soc. J.*, 1857, **10**, 211; *Proc. Roy. Soc.*, 1857, **8**, 495).

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But one research on alcohols can be directly connected with Hofmann's name, that on allyl alcohol, which he carried out in conjunction with Cahours (*Phil. Trans.*, 1857, 575—600). Shortly before this was commenced, Berthelot and de Luca, by subjecting glycerin to the action of phosphorus iodide, had obtained "iodopropylene,"* from which they—and also Zinin—had prepared a sulphocyanate identical with natural oil of mustard; Redtenbacher had previously prepared acrolein and acrylic acid, and the relation of these compounds to the oils of garlic and mustard had been established by the observations of Will and Wertheimer, and of Berthelot and de Luca; bromopropylene had been prepared by Captain Reynolds in Hofmann's own laboratory, and he had himself prepared chloropropylene: an almost complete series of derivatives of the radicle $C_6H_5^*$ was therefore known. But, to quote a passage from the joint paper, which clearly bears the impress of Hofmann's style—

"There yet remained the keystone to be inserted into this edifice; in other words, there was to be discovered the alcohol to which not only all the preceding compounds could be referred, but which might serve in producing a long series of substances analogous to the host of compound ethers derived from common alcohol."

Hofmann and Cahours fully describe the preparation and properties of allyl alcohol and of a considerable number of allyl derivatives, among others the sulphide, which they show to be identical with natural garlic oil.

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Hofmann (in conjunction with Cahours) was not only the discoverer of an unsaturated alcohol which was the first of its kind, and to

* Called *allyl* for the first time, in their communication, by Hofmann and Cahours.

which special interest still attaches on account both of its relation to glycerol and the very limited number of such alcohols; he also discovered sorbic acid, $C_6H_8O_2$, a crystalline, unsaturated acid of the $C_nH_{2n-3}.CO_2H$ series, which has since been the subject of much interesting inquiry. This acid was prepared from the volatile oil obtained on distilling unripe mountain ash berries with steam (*Chem. Soc. J.*, 1860, **12**, 43); judging from Fittig and Barringer's observations (*Liebig's Annalen*, 1872, **161**, 307), the oily parasorbic acid which Hofmann separated from the crude oil by distillation, and which was converted into the crystalline acid by alkalis and acids, was but impure sorbic acid, and not an isomeride, as was long supposed.

An observation of interest to which he drew attention in 1850 (*Chem. Soc. J.*, **3**, 181) should be here referred to, viz., that cinnamic acid, unlike its inferior homologue, benzoic acid, passes unchanged through the animal system.

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The observation which led Griess to his great discovery of the diazo-compounds was made in Kolbe's laboratory in Marburg, and was briefly described in *Liebig's Annalen* (**106**, 123) early in 1858, under the title "Vorläufige Notiz über die Einwirkung von Salpetriger Säure auf Amidinitro- und Aminotrophenylsäure." But the paper in which he first drew attention to the fact that he had established a *new mode of reaction* of nitrous acid was communicated to the Royal Society on December 9, 1858, by Hofmann, whose assistant he then was, the term diazo-derivative being here used for the first term. Although, as Hofmann has told us, the latter paper was a translation of that in the *Annalen*, it is distinctly more explicit. Hofmann may be said to have himself almost missed the discovery of the peculiar behaviour of primary benzenoid amines towards nitrous acid, as his attention was directed to its action on aniline as early as 1850 (*Chem. Soc. J.*, **3**, 231). Sterry Hunt had stated in 1849 that nitrous acid converted aniline into phenol, but his experiments were only of a qualitative character. Hofmann repeated his observations and confirmed them, but only succeeded in obtaining satisfactory results by using aniline hydrochloride and silver nitrite. On subjecting aniline mixed with nitric acid to the action of nitric peroxide, in the manner originally proposed by Piria—who was the first to submit amido-compounds to the action of nitrous acid—he obtained a brown, resinous mass, from which, however, he separated the till then unknown (ortho)nitrophenol, the properties of which he more fully described several years afterwards (*ibid.*, **10**, 203). A number of observations on the action of nitrous acid on ethylamine and its homologues are recorded in this paper.

In the course of his researches on the polyammonias (*Proc. Roy.*

Soc., 1860, **10**, 495), Hofmann made use of the "beautiful mode of substituting nitrogen in the place of hydrogen, lately discovered by P. Griess," at the time when he was seeking for benzenoid diamines, in studying the compound Gottlieb had prepared by partially reducing dinitraniline, then known as nitrazophenylamine, but which, in his opinion, was probably a nitrophenylenediamine, a view confirmed by the result he obtained. It is noteworthy that the product—as Hofmann pointed out—differed in many respects from those obtained in a similar way from other nitrogenous substances, especially in exhibiting remarkable stability; this is readily understood now that we are acquainted with condensation products formed from orthamidodiazocompounds.

In a note on isatin, published in 1861 (*Chem. Soc. J.*, **13**, 73), attention was drawn by Hofmann to the extreme facility with which this substance is converted into nitrosalicylic acid by nitrous acid.

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It will be remembered that, in his earliest research, Hofmann made an important use of chloranil (tetrachloroquinone) in establishing the identity with aniline of the substances described as benzidam, &c. In his second paper he tells us that he was induced by—

"The close relation subsisting between the aniline and phenyl series to try whether chloranil could not be obtained from different members of this group of bodies. . . ."

Phenol, and a number of other substances, were subjected to the action of hydrochloric acid and chlorate of potash. It is noteworthy that the production of chloranil from phenol in this manner was described in a paper read to our Society on December 2, 1844 ("Remarks upon Chloranil," *Chem. Soc. Memoirs*, **2**, 226), which was the first he communicated to us. Attention may be directed to the final paragraph of the paper, as it shows that he had not only recognised the relation of chloranil to quinone, but had also formed views as to the relationship of the latter to aniline—

"In concluding, I wish to call the attention of chemists to the application of chlorate of potash as an oxidising agent, for up to the present time it has been but seldom employed in organic chemistry, and yet the study of its action might, in many cases, lead to very remarkable results. I have treated *kinone*, which has lately become so interesting, in a similar manner to what has been stated, and found that it was transformed with the greatest facility into chloranil. In a future paper this subject will be examined more closely, and at the same time I shall throw out some hints concerning the relations of *kinone* to aniline, a base from which it can likewise be produced."

The promise here made was never fulfilled. It is somewhat remarkable, therefore, that almost the last paper Hofmann published before

leaving England was a "Note on Kinone" (*Proc. Roy. Soc.*, 1863, **13**, 4). In this he pointed out that quinone was easily formed on oxidising (para)phenylene diamine; and that aniline gave an appreciable amount of quinone on oxidation, and benzdine a theoretical yield. The action of aniline on quinone and on chloranil was studied by him at this time, and the results he obtained in the latter case led him to correct Hesse's previous observations on the subject.

Baeyer having suggested that quinone might be derived from 2 mols. of benzene, Hofmann was led to determine its density, and to prove for the first time that it was correctly represented by the formula $C_6H_4O_2$ (*Ber.*, 1870, **3**, 583).

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Hofmann's contributions to inorganic chemistry were remarkably few. In this connection a note may be referred to "Sur le Bromure de Titanium" (*Compt. rend.*, 1856, **42**, 352), in which the preparation of this substance by Duppa is recorded. It is one only of a number of instances in which Hofmann's interest in Kopp's generalisations on boiling points is manifest. The note also serves to recall the time when the atomic weight of silicon was undecided, and its chloride bore the formula $SiCl_3$.

In describing the use of pentachloride of antimony in the preparation of chlorine compounds as a carrier of chlorine (*Chem. Soc. J.*, 1861, **13**, 62), he drew attention to the remarkable action of this substance on carbon bisulphide, from which it simply displaces the sulphur in the manner represented by the equation $CS_2 + 2SbCl_5 = CCl_4 + 2SbCl_3 + 2S$, a small quantity only of sulphur chloride being formed by the action of the pentachloride on the separated sulphur.

He by no means neglected analytical chemistry. The method used in qualitative analysis of separating cadmium from copper, based on the solubility of cadmium sulphide in dilute sulphuric acid, was devised by him. The separation of arsenic from antimony also engaged his attention (*Chem. Soc. J.*, 1861, 78). A number of complete analyses of English mineral waters were made under his direction, and in conjunction with Graham and Miller, in 1851, he made a memorable report to the Secretary of State for the Home Department, on the supply of water to the metropolis (*Chem. Soc. J.*, **4**, 375). He also took part in many other important public inquiries. Of these may be mentioned that into the alleged adulteration of pale ale by strychnine, in conjunction with Graham, in 1852; the elaborate report upon original gravities, in conjunction with Graham and Redwood, published in our Journal, in 1853; and that on the subject of lighting picture galleries by gas, in conjunction with Faraday, Tyndall, Redgrave and Fowke. It was in connection with this last inquiry

that he used triethylphosphine in detecting the presence of carbon bisulphide in coal-gas.

A report which he made to De la Rue & Co. in 1858, on vegetable parchment, published at the time in the *Pharmaceutical Journal* (18, 273) and in *Liebig's Annalen* (112, 243), is historically interesting, especially as specimens are attached to the paper in the latter journal.

Experiments which he made on the changes which guttapercha undergoes under tropical influences, for the purposes of a report on this subject to the Director General of Telegraphs in India, are briefly described in a note in the *Society's Journal* for 1861 (p. 87).

The use of gaseous fuel in the laboratory naturally engaged his attention. The combustion furnace with perforated cylindrical clay burners which he ultimately devised is probably the most efficient yet constructed, although it suffers under the disadvantage that the temperature cannot be quickly varied, as it can be in the more modern forms of furnace in which the Bunsen burner is used.

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To pass to the consideration of Hofmann's work after he left England—full of interest and important as were many of the investigations he carried out, in comparison with that of his earlier years it may not unfairly be characterised as in a measure discursive; and it could not well be otherwise. Another opportunity such as had been afforded him at the outset of his career, and of which he had availed himself with such extraordinary success, was scarcely likely to present itself. Having determined the nature of the amines and alkaloids generally; having discovered the substituted ammoniums; in the field in which he had laboured with such perseverance, there was little left for him to do, he had so fully established the dominant properties of aminoid nitrogen.

A practically complete account of his English work is to be found in the 170 papers indexed under his name in the third volume of the Royal Society's *Catalogue of Scientific Papers*, published prior to 1864. In subsequent volumes the number is raised to 319, but these carry the record only up to the end of 1883. The volumes of the *Berichte* published after this date contain, however, only about 40 communications bearing his name.

Some of his work was based on casual, almost chance, observations; some was the outcome of opportunities such as he was always ready to avail himself of without loss of time; but the greater part naturally consisted in extending and elaborating observations made during his earlier work.

That he entered on his new career at a critical moment is clear from his own statements. Nothing shows this better than the picture

he paints in the preface to his *Introduction to Modern Chemistry*, dated March 24, 1865, in the following striking passages—

“No chemist will need to be reminded, that during the last quarter of a century the science of chemistry has undergone a profound transformation ; attended, during its accomplishment, by struggles so convulsive as to represent what, in political parlance, would be appropriately termed a Revolution.

“Amid continual accessions of fact, so rapid, so voluminous, and so heterogeneous, as almost to exceed the grasp of any single mind, chemical science has been in travail, so to speak, with new laws and principles of co-ordination, engendered, perhaps, partly by the sheer force of their own deeply felt necessity, but partly, also, and mainly, due to the powerful initiative impulsion of a few philosophical master-minds.

“Based on the concurrent examination of the volumetric and ponderal combining ratios of certain typical elements, and on the recognition, in their standard combinations, of a few well marked structural types, these principles have introduced into the domain of chemistry the pregnant idea of *Classification*—the conception of a series of natural *Groups*, resembling the genera of the biological sciences, and culminating in the establishment of an orderly system, where before there had seemed to be but a chaos of disconnected facts.

“Under the influence of these and certain other cognate ideas, new views have arisen as to the constitution and chemical properties of matter ; a reformed chemical notation has thence of necessity ensued ; and structural relations, previously unsuspected, have disclosed identity of parentage in compounds till then deemed utterly diverse.

“It appears to be wisely ordered in scientific as in social affairs, that the innovating spirit which belongs to youth has its check and counterpoise in the conservative tendency essentially characteristic of age ; so that, in the sharp collision of these rival force, new principles of any kind find a sort of fiery ordeal interposed between their first enunciation and final acceptance ; doubtless the appointed test of their soundness and vitality.

“Hence the domain of chemical philosophy has, for many years past, rather resembled a tumultuous battle-plain than a field bestowed by nature for peaceful cultivation by mankind. The new ideas springing up of necessity one by one, and not always free, at their first conception, from errors and inconsistencies, have been resisted by the champions of the old chemical dogmas, as a gratuitous revolt against established authority. Controversy has naturally stimulated research, which, in its turn, has produced rapid modifications of theory ; so that the aspect of chemistry has been in a state of incessant change. It is, indeed, only within the last few years that the new doctrines have acquired a logical consistency, and a consequent ascendancy throughout Europe, acquiring at length, for our long agitated science, a period of comparative calm.

“The author's lot, both as a student and as a teacher, has been cast amidst the storms of this controversial period ; in which he has felt it his duty to take part on the side of innovation.”

Again, in the speech which he delivered on taking his place as a

member of the Berlin Academy of Sciences in succession to E. Mitscherlich—an event which coincided with his return to Germany—he refers to the previous 25 years as a memorable period in the history of our science, during which the new discipline—the work of Liebig's creative genius—Organic Chemistry had acquired an extraordinary importance, so that

“Wo gestern kaum der Wald gelichtet war, erhob sich heute schon eine prächtige Stadt mit grossen Plätzen und weitauslaufenden Strassen und noch viel weiter gehendem Zukunfts-Bauplan.”

He then briefly recalls the struggles which had been the natural outcome of the activity everywhere displayed by chemists in bringing new facts to light, facts which could not well be interpreted by means of the rudimentary theories inherited from mineral chemistry; and after referring to the importance which the study of volumetric relationships had acquired during the previous decade, he describes the gradual manner in which he himself became a convert to the views of the Gerhardt school. He then tells us what he regarded his mission to be at this time—

“Ob und in wie weit meine Arbeiten zur Entfaltung dieser Schule ihr Schärfelein beigetragen haben, darüber erlaube ich mir kein Urtheil, wohl aber bekenne ich gern und frei, dass ich in ihren Lehren die mächtigsten Anregungen zu neuer Forschung, die willkommensten Fingerzeige für richtige Beurtheilung beobachteter Erscheinungen, endlich den einfachsten Ausdruck für die Darstellung gewonnener Resultate gefunden habe. In der That sind die Vortheile dieser Darstellungsweise so gross, die Kraft und Zeitersparniss für den Lernenden sowohl als für den Lehrer so bedeutend, dass es mir, und zwar namentlich auch in meiner neuen Stellung als Akademiker, eine Pflicht ist zur allgemeinsten Verbreitung der Anschauungen der modernen Chemie in weitestem Umfange nach besten Kräften mitzuwirken. Obwohl Fast überall anerkannt, sind doch diese Anschauungen noch sehr weit davon entfernt zu allgemeiner Geltung und namentlich zur alltäglichen Gebrauch in der Schule gekommen zu sein. Hier bleibt noch unendlich viel zu thun übrig. Die Ausbildung des neuen Systems für die Zwecke des Unterrichts ist eine Aufgabe, die bis jetzt erst sehr lückenhaft gelöst ist. In den Grenzgebieten, auf denen die Chemie anderer Disciplinen die Hand reicht, sind die Wellen der mächtigen Brandung, die sich im engeren Kreise unserer Wissenschaft selbst schon wieder zu beruhigen beginnen, nur erst gang schwach fühlbar geworden, in einigen sind diese Wellen noch gar nicht angelangt. Auch in diesem Sinne ist daher der Thätigkeit weiter Spielraum geblieben.” (*Monatsbericht*, June, 1865.)

Such were Hofmann's views in 1865, but advance was to take place more rapidly than he had foreseen, and even he was to be left behind to some extent. It is a matter of common knowledge how, at this time, the undoubtedly inelastic theory of types became merged in a wider generalisation—the modern theory of structure.

Kekulé's genius gave birth to the benzene theory, our present views on valency crystallised out suddenly from the somewhat confused magma in which they had been overlooked, and a revolution was silently, almost immediately, effected—development rapidly taking place along lines already well marked out by Frankland and Kolbe, but which for a time had been obscured by the attractive simplicity of the theory of types. Hofmann, however, seems never to have thoroughly entered with full sympathy into the spirit of the new chemistry, and rarely adopted the modern style in his writings.

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His researches on colouring matters, which are a very important part of his later work, have already been so fully considered by Dr. Perkin that it will not be necessary again to refer to them here.

The first investigation of which an account was published after his return to Germany dealt with a class of diamines till then almost unknown but which have since acquired considerable importance, the so-called *amidines* (*Monatsber. Akad., Berlin*, 1865, 649; *Proc. Roy. Soc.*, 1867, 55). It was the outcome of a chance observation. A quantity of acetanilide required for the study of the chloro-, bromo- and nitro-derivatives of aniline had been prepared by means of acetyl chloride, and in seeking to recover the unattacked aniline a crystalline base was discovered of the formula $\text{CH}_3\text{C}(\text{NPh})\text{NHPh}$. The production of this compound was traced to the presence in the acetyl chloride of phosphorus trichloride, and to the action of this substance on acetanilide and aniline conjointly. The new base was recognised as a homologue of the formyldiphenyldiamine which he had prepared many years before from chloroform and aniline; and on substituting formanilide* for acetanilide the formyl-diamine was obtained without difficulty. Benzanilide and several other anilides were converted into similar compounds.

Hofmann did not fail to recognise that the new bases were related to the *acediamine* which Strecker had obtained from acetamide by the action of gaseous hydrogen chloride, and years afterwards, when the formation of this compound was called in question by Tawildarow, he showed that it could be prepared without difficulty by following Strecker's directions (*Ber.*, 1884, 17, 1954).

But the paper under consideration specially deserves attention on account of the very important foot-note that occurs in it in which the systematic nomenclature for hydrocarbons and hydrocarbon radicles since so extensively used is suggested. It was here that Hofmann first proposed to adopt names indicating the number of carbon atoms

* The production of a metallic derivative on adding strong caustic soda lye to a solution of formanilide was first called attention to in this paper.

in the compound, and to terminate the names of the hydrocarbons of the paraffin series in *ane*, and those of other series in *ene*, *ine*, &c.

In accordance with this system, the bases he prepared from form-anilide, acetanilide and benzanilide were termed *methenyl*, *ethenyl* and *benzenyl-diphenyldiamine* respectively.

Many similar cases of the formation of bases by dehydration have since been studied, and especially the anhydro-bases formed by the withdrawal of the elements of water from benzenoid orthamido-derivatives now constitute an important class of compounds; in most cases, however, these are not of the same type as those studied by Hofmann, inasmuch as the withdrawal of water involves the formation of a secondary ring.

In 1888 (*Ber.*, 21, 2332), Hofmann himself showed that the formation of such cycloid anhydro-bases was not confined to benzenoid compounds, but that they could be prepared equally well from ethylene- and propylene-diamines, and even from trimethylene-diamine; for example, that diacetylenediamine was converted on distillation into the acetate of the anhydro-base represented by

the formula
$$\begin{array}{c} \text{CH}_2 \cdot \text{N} : \text{C} \cdot \text{CH}_3 \\ | \\ \text{CH}_2 - \text{NH} \end{array}$$

With the object of preparing formanilide for further experiments on the methenyl base, as it was difficult to obtain formic acid in quantity at that time, Hofmann resorted to the old method of distilling the oxalate of the amine, and in establishing the conditions which gave rise to the best yield he was led to take note of the various bye-products. On boiling the crude distillate with muriatic acid, a considerable quantity of benzonitrile was found to distil over; as this was evidently derived from the formanilide, it appeared probable that the method might be made use of for the preparation of the nitriles of other acids which were either procurable with difficulty or unknown. Succeeding with toluidine, he at once passed to naphthylamine, and obtained for the first time the nitrile of naphthoic acid.

Naphthyl cyanide, the corresponding amide, the thioamide, the amine formed by reducing this last, and the acid and a number of other derivatives were fully described in two subsequent papers (*ibid.*, 16, 300, 445). It should be mentioned that it is shown in the last of these that the thioamide is very much more easily reduced than is the nitrile.

It may be added that this work was carried out by an English assistant, our distinguished Fellow, Mr. C. O'Sullivan, who had accompanied him to Germany.

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Hofmann's activity at this period was extraordinary: at the end of the summer of 1867 he communicated to the Berlin Academy two discoveries of fundamental importance—that of a method of preparing the isonitriles homologous with hydrogen cyanide, and that of formic or methaldehyde; accounts of the discoveries were also forwarded to the Royal Society, reaching it during the recess. Their history is best related in his own words—

“The aldehyde of the methyl series is not known; all the chemical manuals say so, and for the last 20 years my students have been duly informed thereof. It will scarcely appear strange that more efforts to become acquainted with that body should not have been made, since the masterly picture which Liebig has delineated of the aldehyde *par excellence* embraced as it were the history of the whole class, and of course also of the aldehyde in question. Nevertheless, methylic alcohol deserves our attention for more than one reason. As one of the simplest terms of the monocarbon series, occupying a position intermediate between marsh gas and carbonic acid, as a link of transition connecting methylic alcohol and formic acid, as either aldehyde or acetone, according to the point of view from which we look upon it, the compound CH_2O illustrates a greater variety of relations than any one of the higher aldehydes. But in addition to the interest with which the methyl compound has thus always been invested, this substance possesses special claims upon our attention at the present moment. Our actual method of treating organic chemistry for the purposes of instruction almost involves the necessity of starting from the methyl series. The simplest of aldehydes thus acquires quite an especial importance, and all those who, like the author of this note, are engaged in teaching, cannot fail to have sadly missed a compound which is the carrier of such varied and interesting considerations.

“The desire which I have frequently felt in my lectures of developing the idea of the genus aldehyde, when speaking of the methyl compounds, has more than once induced me to attempt the preparation of methyl aldehyde, but it was only at the conclusion of my last summer course that I succeeded, to a certain extent at all events, in attaining the object of my wishes.

“A substance possessing the composition and the properties of methylic aldehyde is formed with surprising facility if a current of atmospheric air charged with the vapour of methylic alcohol be directed upon an incandescent platinum spiral (*Proc. Roy. Soc.*, September, 1867, 16, 156).”

This passage is eminently characteristic of Hofmann's picturesque and comprehensive style, overflowing always with the sense of the importance of the subject which he is considering, whatever its nature.

Proof that methylic aldehyde was produced in the manner described* was obtained, not by the actual isolation of the substance,

* The amount produced, as Hofmann subsequently showed (*Ber.*, 1878, 11, 1685), by using a mere spiral of platinum wire, is very small—not exceeding 1 per cent. By substituting a bundle of platinum wires enclosed in a platinum tube, the

but by the preparation from the crude liquid product by the action of sulphuretted hydrogen of a crystalline compound giving numbers on analysis corresponding with the formula CH_2S .

In two later notices (*Ber.*, 1869, **2**, 152; 1870, **3**, 584) Hofmann showed that this thio-compound was identical with the substance previously prepared by Girard by the action of nascent hydrogen on carbon bisulphide, and by Husemann from methylene iodide and potassium sulphide. He also discovered that although the aldehyde is gaseous, it very readily undergoes conversion into a solid polymeride identical with the dioxymethylene previously obtained by Butlerow from methylene iodide; this substance is depolymerised when heated, the gas obtained from it being the aldehyde, but on cooling the gas, it soon returns to the solid state. The solid thio-aldehyde, however, volatilises unchanged, its vapour density agreeing with the formula $\text{C}_3\text{H}_6\text{S}_3$, corresponding to that of the thio-aldehyde prepared from ordinary aldehyde.

Butlerow had converted the "dioxymethylene" he prepared into a sugar-like substance, and when Baeyer, soon after Hofmann's discovery of the aldehyde, specially called attention to the probability that formic aldehyde was an initial product of assimilation in plants, it became an object of the greatest interest to chemists. But it was not until several years afterwards that Loew, having much improved the method of preparing the aldehyde, corroborated and extended Butlerow's observation, and established the fact that a substance of the composition of glucose was formed by the condensation of the aldehyde under the influence of alkalis. All know how Emil Fischer, in the course of his marvellous researches on the carbohydrates, eventually proved that the synthetic product consisted of equal proportions of ordinary glucose and its isomeride of equal opposite rotatory power.

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Although the discovery of the isonitriles was in a sense accidental, it well illustrates Hofmann's highly developed acumen and readiness to seize any opportunity. In describing it (*Proc. Roy. Soc.*, 1867, **16**, 144) he says—

"In a lecture, I wanted to exhibit the interesting transformation of ammonia into prussic acid by means of chloroform, which was first observed by M. Cloez, and which illustrates so well our present views on quantivalence. When the two substances alone are allowed to act upon one another, this

amount was raised to 5 per cent. ; and by distilling off methylic alcohol, and freeing out water from the residue, it was increased to 10 per cent. The method was subsequently so much improved by Loew and by Tollens, that it became possible to prepare solutions containing 30—40 per cent. of the aldehyde (*Ber.*, 1886, **19**, 2133).

reaction can be rapidly accomplished only at a high temperature, and consequently under pressure. In order to shorten the process (in one word, in order to exhibit this important reaction in a lecture experiment), I had added potash to the mixture for the purpose of fixing the newly formed prussic acid, and was delighted to find that a few seconds ebullition was sufficient to yield a considerable amount of cyanide of potassium, so as to furnish, after the addition of the two salts of iron, a large quantity of Prussian blue. On subsequently repeating the experiment with some of the derivatives of ammonia, more especially with several primary monamines, I was astonished to observe in each case a powerful reaction, giving rise to the evolution of vapours of an almost overwhelming odour, strongly recalling that of prussic acid. But few experiments were necessary for the purpose of isolating the odoriferous body. The compounds thus formed are the substances isomeric with the hydrocyanic ethers or nitriles hitherto examined."

We read further

"The facility of procuring the necessary material, as well as old predictions, suggested the phenyl series as the one to be examined in the first place."

Less than a fortnight after the account of the cyanide of phenyl was sent to the Royal Society, he forwarded a second communication in which he states

"I have followed up the study of these new bodies, which have become more and more attractive to me in proportion as I investigated their nature."

Only Hofmann could write in this way of substances having such intolerably nauseating properties, "the penetrating odour of which," to use his own words with reference to the ethyl compound, "surpasses anything that it is possible to conceive."

The investigation came at the close of the session, and was carried on during the summer, at the end of August; and even those who never knew the man and his insatiable appetite for results, can picture to themselves what must have been his anxiety to learn more of such remarkable substances when they read, with reference to the ethyl compound—

"As the substance is rather volatile, the frequently repeated fractional distillations became a most painful operation, and more than once, while I have been engaged in these experiments, my laboratory has been almost inaccessible. Thus with a temperature of 20° I have found it desirable to interrupt, for the time, the preparation in the pure state of the cyanide of ethyl, and to resume it at a more favourable season!"

But he was not to be balked of his prey, for he continues—

"I was, nevertheless, curious to study, even now, a true homologue of cyanide of ethyl in order to compare its properties with those of cyanide of phenyl. The boiling points of the amylic compounds being within con-

venient limits, I was induced to select the amyl series as presenting the greatest chance of success."

A week later (September 7th) yet a third note on the same subject came to the Royal Society. In this Hofmann drew attention to the fact that the isocyanides are formed along with the nitriles on distilling the sulphovinates with potassium cyanide—hence the intolerable odour of the crude product, so different from the agreeable odour of the nitriles; he also pointed out that E. Meyer, many years before, had allowed the ethyl compound to pass through his hands unrecognised, as by heating silver cyanide with ethyl iodide and distilling the product he had obtained a liquid having an overwhelming odour, and yielding ethylamine on hydrolysis.

Meyer had observed that the cyanide formed a compound with the silver cyanide. This Hofmann verified in the case of the amyl isonitrile; he only succeeded in separating the amyl cyanide by subjecting the double cyanide to dry distillation. Speaking of the silver cyanide process, he remarks—

"In the latter process, many secondary products are obtained, but by a more complete study, perhaps, it may be modified so as to diminish their quantity."

Hofmann was unaware at this time that he had been anticipated in the discovery of the isocyanides by Gautier, as only a brief reference to this chemist's results had been published. By distilling the double cyanide produced by the interaction of the alcoholic iodide and silver cyanide with potassium cyanide, Gautier obtained an almost theoretical yield of the methyl and ethyl compounds; thus effecting the modification of the method which Hofmann had spoken of as necessary to diminish the amount of secondary products.

An interesting compound—half nitrile and half isonitrile—was prepared by him from amidobenzonitrile in 1868 (*Ber.*, **1**, 194).*

In a brief note published in 1870 (*Ber.*, **3**, 766), he pointed out that the compounds formed by the union of triethylphosphine with mustard oils were resolved into the isocyanide and triethylphosphine sulphide when heated under pressure.

Although little was published by him during the next 10 years having reference to this class of compounds, they continued to occupy his attention; but, as he tells us at the outset of a communication on the action of sulphuretted hydrogen on the isonitriles (*Ber.*, 1877, **12**, 1095), he had always been obliged, whenever he again engaged in such work, to soon desist, as he could not ask those who assisted him to endure for long their almost unbearable odours.

* In the paper in which this is described attention is drawn to the remarkable manner in which nitrobenzonitrile is reconverted into benzonitrile by the action of reducing agents.

He speaks also of the "wahrhaft opfermuthigen Beistand" afforded him in the course of the experiments.

The object in view in subjecting the isonitriles to the action of sulphuretted hydrogen was to obtain thioamides from which thioacids might be prepared, especially thioformic acid. Phenyl isocyanide was found to be gradually acted on and converted into thioformanilide; experiments to substitute for the pure cyanide the crude product obtained on mixing chloroform, aniline and alcoholic potash were but partially successful, much methenyldiphenylamidine being also formed.

As thioformanilide dissolves in a cold dilute solution of an alkali without undergoing change, Hofmann represented it by the formula $\text{NHPh}\cdot\text{C}(\text{SH})$.

On the appearance of this paper, Berntsen pointed out that amides might be prepared by heating amidines with sulphuretted hydrogen. Hofmann, in consequence, extended his observations, and showed that acid amides were converted into corresponding thioamides by distillation with phosphorus pentasulphide (*Ber.*, 1878, **11**, 338).

As new amines came into his hands, he could rarely resist the temptation of fully exploiting their powers of affording new compounds—the mere production of which appears at all times to have given him infinite pleasure—and of preparing the corresponding isonitrile among others. Thus, in 1884 (*Ber.*, **17**, 1914), he prepared the isonitrile from the tetramethylaniline, and in the next year (*Ber.*, **18**, 1821), that from the pentamethylaniline which he obtained in the course of the investigation of the products formed on heating aniline hydrochloride with methyl alcohol. Both are described as crystalline solids: the former as possessing the frightful odour characteristic of the phenyl compound in a but slightly diminished degree; the odour of the latter—on account of its slight volatility (m. p. 168°)—as far from being so overpowering as that of the lower homologues. Both undergo change with extreme readiness when heated—the former on distillation, the latter when heated slightly above its melting point—yielding the isomeric nitriles; these latter, on the other hand, are compounds of most remarkable stability which cannot be converted into acids by any of the methods ordinarily adopted in hydrolysing nitriles.

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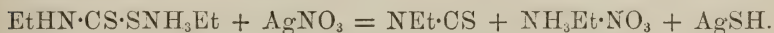
Phenylic (iso)cyanate, $\text{Ph}\cdot\text{N}:\text{CO}$, it will be remembered, was discovered by Hofmann in 1849 among the products of the complex action taking place on distilling melanoximide (oxalyldiphenylguanidine). In the third of his notes of researches on the poly-ammonias, communicated to the Royal Society in May 1858 (*Proc. Roy. Soc.*, **9**, 274), a more rational method of preparing this and the until then unknown,

analogous thio-compound was described, which consisted in subjecting carbanilide and sulphocarbanilide to the action of agents such as phosphoric anhydride capable of fixing aniline. The method was soon afterwards applied in the naphthyl series, at his suggestion, by Vincent Hall (*ibid.*, 1858, 9, 365).

Ten years later, Hofmann's first communication to the Berlin Society (*Ber.*, 1868, 25) was the forerunner of a series (*Ber.*, 1868, 169, 201; 1869, 116, 452) in which improved methods of preparing the thiocyanates analogous with mustard oil were described as well as a number of interesting derivatives formed from them.

In the course of these communications he showed that the method by which he had first prepared the phenyl analogue of mustard oil, $\text{PhN}:\text{CS}$, was of general application—that is to say, that the mustard oils could be obtained by combining a primary monamine, NH_2R , with carbon bisulphide; then expelling sulphuretted hydrogen from the thiocarbamate, $\text{NHR}:\text{CS}:\text{SNH}_2\text{R}$, by heating its solution, so converting it into the thiourea, $\text{NHR}:\text{CS}:\text{NHR}$; and finally distilling this urea with phosphoric anhydride.

An even simpler method consisted in boiling the solution of the thiocarbamate formed from carbon bisulphide and the monamine with an equivalent proportion (not an excess) of a metallic salt such as silver nitrate or mercuric chloride, the latter being that best suited for practical use—



Secondary as well as primary fatty amines, but not tertiary, may thus be converted into mustard oils, a mercaptide being formed in place of the sulphhydrate when the thiocarbamate of the secondary amine is decomposed. In the case of benzenoid thiocarbamates, change at once takes place spontaneously into sulphuretted hydrogen, mustard oil and amine, and the latter then interact, forming a thiourea which is but slowly acted on by the metallic salt: hence the method is not applicable to the preparation of benzenoid mustard oils.

Yet another method by which mustard oils could be prepared, disclosed by this investigation, consisted in adding an alcoholic solution of iodine to the alcoholic solution of the thiocarbamate, *e.g.*,



Three of the four isomeric butyl mustard oils, crotonyl mustard oil and angelyl mustard oil were subsequently prepared by him, the two latter from bromobutylene and bromamylene respectively (*Ber.*, 1874, 508, 514; 1879, 990).

The mustard oils were shown by Hofmann to be all readily acted on by water, by alcohols and by mercaptans, the two last forming

hemithio- and thio-urethanes—ethereal salts of thiocarbamic acids—respectively.

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Full use was soon made of the new method of preparing mustard oils. Experiments on the action of chlorine on phenyl mustard oil, carried out in his laboratory by Sell and Zierold (*Ber.*, 1874, 1228), had led to the discovery of an isocyanophenylic chloride, $C_6H_5 \cdot NCCl_2$. It was probable that this would be more readily prepared by the action of phosphorus pentachloride. Hofmann found (*Ber.*, 1879, 1126) that although it could be produced in such a manner, what appeared from its composition to be a simple chloro-derivative was also formed; but this had none of the properties of a mustard oil, and readily exchanged its chlorine for OH, NH_2 , &c.; moreover, it was not identical with any one of the mustard oils obtained from the three chloranilines.

A variety of derivatives were prepared from this compound; on reduction it afforded a substance isomeric with both phenyl mustard oil and phenyl thiocyanate (*Ber.*, 1880, 8).

The behaviour of phenyl mustard oil with other chlorides was then studied: on heating it with benzoyl chloride a very small amount of what appeared to be a phenylated mustard oil was obtained. In the course of experiments made with the object of preparing this substance in larger quantity, benzanilide was heated with sulphur. The product proved to be identical with that prepared from the mustard oil and benzoylchloride, and was soon recognised as a member of a class of orthamido-derivatives of which a number had been obtained at about that time, viz., as $C_6H_4 \begin{smallmatrix} N \\ \diagup \diagdown \\ S \end{smallmatrix} CPh$, corresponding to the compound prepared by Ladenburg from orthamidophenol and benzoyl chloride, than which, however, it was much more stable. On fusion with alkali it was resolved into amidophenylmercaptan and benzoate, and was reproduced from the former by the action of benzoylchloride (*Ber.*, 1879, 2359).

The amidophenylmercaptan produced in this manner was shown to be the ortho-compound by preparing it from orthonitrobenzenesulphonic acid.

The compound originally obtained was thus shown to have the constitution represented by the formula $C_6H_4 \begin{smallmatrix} N \\ \diagup \diagdown \\ S \end{smallmatrix} CCl$. The corresponding base was easily prepared from amidophenylmercaptan and formic acid, and a number of homologous compounds from the mercaptan and the acid chlorides (*Ber.*, 1880, 8).

Hofmann subsequently made experiments with the object of ascertaining whether the method used in preparing the phenylated com-

pound could be applied to other amides (*Ber.*, 1880, 1223). On heating formanilide with sulphur, a very small amount of the methenyl base was obtained.

Acetanilide, however, was found to behave in an altogether peculiar manner, giving rise to the "oxalyl" compound represented by the formula $C_6H_4\langle\begin{smallmatrix} N \\ S \end{smallmatrix}\rangle C-C\langle\begin{smallmatrix} N \\ S \end{smallmatrix}\rangle C_6H_4$.

Although no satisfactory explanation of the nature of the change could be discovered, this formula was placed beyond question by the production of the compound in a great variety of ways; *e.g.* (1) by the action of zinc on the chlorinated methenyl base, (2) by the interaction of the methenyl base and its chlorinated derivative, and (3) by the action either of oxalic acid (in presence of phosphorus trichloride), or of oxalic ether, or of cyanogen on amidophenylmercaptan. Moreover, it was shown that the compound was converted by hydrolysis into oxalic acid and amidophenylmercaptan.

The same substance was obtained on using propionanilide, but a homologous compound was formed from succinamide.

A great number of experiments were made by him, both at this time and several years afterwards (*Ber.*, 1887, 1788, 1798, 2251), in which amidophenylmercaptan was subjected to the action of a variety of substances—acids, aldehydes, &c. In almost every case derivatives of the compound $C_6H_4\langle\begin{smallmatrix} N \\ S \end{smallmatrix}\rangle CH$ were obtained. He also extended his observations to the corresponding naphthyl compound.

Many of the substances he prepared are of considerable interest. Thus, by the action of cyanogen, keeping the latter in excess, a compound convertible by the action of the mercaptan into the remarkable oxalyl derivative above referred to was obtained which he represented by the formula $C_6H_4\langle\begin{smallmatrix} N \\ S \end{smallmatrix}\rangle C-C\langle\begin{smallmatrix} NH_2 \\ NH \end{smallmatrix}\rangle$; on hydrolysis,

this gave ammonia and the acid $C_6H_4\langle\begin{smallmatrix} N \\ S \end{smallmatrix}\rangle C\cdot COOH$. Hofmann drew attention to the compound prepared by Bladin by the interaction of orthophenylenediamine and cyanogen as being probably analogously constituted.

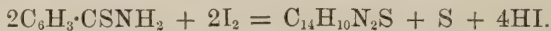
In the last paper of this series, the preparation of amidophenylmercaptan was fully discussed, and attention drawn to its marked unpleasant physiological action on the skin.

Hofmann did not fail to notice that the bases he had prepared from the mercaptan bore a relation to quinoline similar to that which thiophen bears to benzene, and he was not content to merely remark this, but proved that by subjecting them to a treatment similar to that adopted in preparing cyanine from quinoline, cyanine-like substances

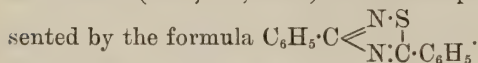
were produced (*Ber.*, 1887, 20, 2262). Cyanine, it is to be remembered, was at this time recognised as the product of the interaction of the amylammonium iodides of homologous quinolines; Hofmann converted both the methenyl and ethenyl thio-base into amyl iodides, and showed that neither of these gave rise to colouring matter when heated alone with alkali, but that a mixture of the two readily afforded a cyanine-like substance corresponding to cyanine in composition. As in the quinoline series, the meth- and eth-iodides gave rise to similar products. Moreover, corresponding naphthyl compounds were prepared; and he showed that not only was it possible to "cross" the naphthyl with the phenyl compounds, but also to cross these with the quinoline compound, but, strange to say, the bases obtained from amidophenol—although strictly analogous to those prepared from the mercaptan—could not be converted into colouring matters, nor could cyanines be formed with the aid of the methiodides of dimethylaniline, dimethylparatoluidine, pyridine or collidine.

Hofmann's intense desire always to carry the argument from analogy as far as it could possibly be pressed, and to garner up every result within reach, is nowhere more strikingly manifest than in the page or two in which these results are described.

Reference may be here made to another investigation in which compounds of the same type as those derived from amidophenyl-mercaptan were obtained by him, viz., to that on the action of iodine on thiobenzamide. As far back as 1869 he had pointed out that the interaction takes place in accordance with the equation



But the nature of the product was not ascertained until 1892, when a paper by Hofmann and Gabriel was communicated to the German Chemical Society at the meeting at which the death of the former was announced (*Ber.*, 25, 1578). The compound was shown to be represented by the formula



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We now pass to one of the most interesting of his later investigations.

Having found a difficulty in preparing phenyl (iso)cyanate in any quantity by distilling diphenylcarbamide with phosphoric anhydride, on noticing that hemithiophenylurethane was resolved into phenyl mustard oil and alcohol by distilling it alone or with phosphoric anhydride, he was led to attempt the preparation of phenyl (iso)cyanate by a similar process from phenylurethane, a substance easily produced by acting on aniline with ethylic chlorocarbonate (*Proc. Roy. Soc.*, 1870, 19, 108). Admirable results were obtained, and the

tolyl, xylyl and naphthyl compounds were equally readily prepared by the method. With reference to these, it is noteworthy that he points out that not only has the xylyl compound a feeble odour, attacking the eyes but slightly, but that it is a remarkably inert substance as compared with the analogous cyanates, including even the naphthyl compound.

Hofmann was never the man to sacrifice an opportunity. Being now in the possession of a method enabling him to prepare phenyl(iso)-cyanate, he is reminded of an interesting old observation that when brought into contact with triethylphosphine it was converted into a crystalline solid, supposed at the time to be the corresponding cyanurate. On re-investigating this substance, he found, however, that it was capable of uniting with alcohol in the proportion of $C_2H_6O : 2NPh \cdot CO$, forming a substituted allophanic ether, and therefore inferred that it was a dicyanic derivative (*Ber.*, 1871, 4, 246).

Finding that substituted biurets were produced by the action of amines on the dicyanate, these observations were soon followed by others on biuret and allied compounds (*ibid.*, 262).

The subject did not again occupy his attention until 1885. He then described experiments showing that no other agent besides triethylphosphine was capable of converting phenyl(iso)cyanate into the dimolecular form before referred to; on heating it with potassium acetate, he obtained the (iso)cyanurate which he had previously prepared from triphenylmelamine (*Ber.*, 1885, 18, 764).

It will be remembered that he had originally obtained melaniline from aniline and cyanogen chloride and carbatriphenyltriamine from aniline and carbon tetrachloride; in the fifteenth of his Notes of Researches on the Polyammonias (*Proc. Roy. Soc.*, 11, 281), describing the production of a triethylcarbatriamine from ethylic cyanurate, he refers to the simple relation which these compounds bear to the guanidine then lately obtained by Strecker. His interest being thus awakened in guanidine, he endeavoured unsuccessfully to prepare it from carbon tetrachloride and ammonia, but succeeded, however, when nitrotrichloromethane (chloropicrin) was substituted for the tetrachloride (*Chem. Soc. J.*, 1866, 19, 249; *Ber.*, 1868, 145).

The study of the action of iodine on diphenylsulphocarbamide, as a means of withdrawing sulphur, subsequently led him to devise a method of general application for the preparation of guanidine derivatives, consisting in the withdrawal of sulphur from a thiourea in presence of an amine (*Ber.*, 1869, 452, 455, 600, 687; 1874, 947).

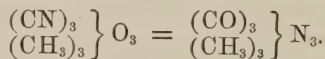
Mention may also be here made of experiments which he instituted on the action of cyanogen on triphenylguanidine with the object of elucidating the formation of a peculiar red bye-product of the action of cyanogen on aniline (*Ber.*, 1870, 764).

In the course of the experiments with thioureas last referred to, observations were made which were followed up with important consequences. On desulphurising ethylthiourea by means of lead or mercuric oxide, a crystalline base was obtained which it was at once perceived might be regarded as a triethyl-derivative of melamine, *i.e.*, "cyanuramide"; but it was soon obvious that the primary product of change was a cyanamide, and that the melamine was formed from this by polymerisation. Hofmann showed that this was the case by producing the compound both from the ethylecyanamide prepared from ethylamine and cyanogen chloride—following the directions originally given by Cahours and Cloez—and from the urea.

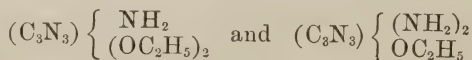
Triphenylmelamine was prepared, in like manner, from phenylthiourea and from phenylcyanamide (*Ber.*, 1870, **3**, 264). It was shown that on hydrolysis these bases exchange amidogen for hydroxyl, ultimately yielding cyanuric ethers.

A tetraphenylmelamine having somewhat peculiar properties (*Ber.*, 1874, **7**, 1736), which he subsequently described, is perhaps appropriately referred to here.

The ethers isomeric with the (iso)cyanic ethers studied by Wurtz had, up to this time, received but slight attention, the ethyl compound alone, prepared from cyanogen chloride and sodium ethylate, having been described by Cloez under the name of *cyanetholine*. As such ethers were to be regarded as analogous in composition to cyanamide, Hofmann and Olshausen were led to think that, like this latter, they would readily polymerise and yield compounds isomeric with the cyanuric ethers. Operating in the methyl series, although they were unable to prepare the cyanate, they obtained a crystalline product yielding cyanuric acid and methyl alcohol on hydrolysis; on distillation, this was converted into the well known (iso)cyanurate—



A corresponding phenyl compound was prepared from sodium phenate and gaseous cyanogen chloride.* On repeating Cloez's experiments, however, they did not succeed in preparing either the true cyanate or the cyanurate, but obtained instead two compounds intermediate between the latter and melamine, *viz.*,



(*Proc. Roy. Soc.*, 1870, 493). The blank was filled up, however, and

* The use of solid cyanogen chloride was subsequently recommended (*Ber.* 1885, 765).

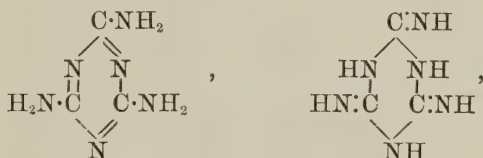
the subject much more fully investigated several years afterwards by Hofmann (*Ber.*, 1886, **19**, 2061).

Meanwhile, however, his attention had been directed to the corresponding sulphur compounds, and he had found that methylthiocyanate (prepared by distilling a mixture of potassium thiocyanate and potassium methyl sulphate) could be converted into a crystalline polymeride giving cyanuric acid and methyl mercaptan on hydrolysis (*Ber.*, 1880, **13**, 1349).

A remarkable series of further communications on this subject was published in 1885. In the first of these it is pointed out (*Ber.*, 2196) that highly purified methyl thiocyanate does not polymerise when heated, although it is partly changed into mustard oil; on adding a few drops of muriatic or sulphuric acid, however, change readily sets in. By heating the methyl thiocyanurate with sodium sulphide, he obtained thiocyanuric acid, which he also prepared from cyanuric chloride and a metallic sulphide.

By heating methyl thiocyanurate with ammonia, he obtained both the intermediate amidothioethers and also melamine; corresponding compounds were prepared with the aid of methylamine, ethylamine, dimethylamine and diethylamine. The action of various amines on cyanuric chloride was also studied very fully on this occasion (*Ber.*, 1885, **18**, 2755). A considerable number of substituted normal melamines were prepared in the course of these experiments, and naturally Hofmann was led to discuss the constitution of melamine and also of the various substituted melamines which he had previously prepared (*Ber.*, 1885, **18**, 2786).

Of the two possible formulæ,



he had no hesitation in attributing the former to melamine itself and the melamine derivatives prepared from cyanuric chloride and the thiocyanuric ethers, the fact that the hexamethylmelamine obtained with the aid of dimethylamine is reconverted into this amine on hydrolysis, as he points out, leaving no room for doubt that it is so constituted. On the other hand, the (iso)melamines obtained from thioureas are to be regarded as derivatives of a different type—as imido- not amido-compounds—being convertible into isocyanuric ethers, which yield amines on hydrolysis.

After fully discussing the constitution of cyanuric acid itself, both on this and on a subsequent occasion (*Ber.*, 1886, **19**, 2084), Hofmann

maintained the opinion that it is probably the hydroxy-compound corresponding to the amido-form of melamine. As an additional argument, he brought forward the fact that, whereas the cyanuric ethers and phosphorus pentachloride interact to form cyanuric chloride, the same agent converts methylisocyanurate into a chlorinated derivative of the formula $C_3O_3N_3(CH_2Cl)_3$ —a remarkable compound which he more fully described in a later paper (*Ber.*, 1886, 2084).

But Hofmann not only recognised the existence of two forms of melamines; it did not fail to strike him that mixed intermediate forms should also exist, and in a later notice, in which a number of observations on phenylated ^{amine}melamines are recorded, he pointed out that an asymmetric triphenylmelamine is actually formed in preparing triphenylisomelamine ^{amine} from phenylecyanamide. Further attention was drawn to the existence of such mixed forms in 1886 (*Ber.*, 2084).

Isothiocyanurates, corresponding to the isocyanurates, formed by the polymerisation of the mustard oils, remained to be prepared—the last paper published in Hofmann's name alone in the *Berichte* (1892, 876) was a brief announcement of their discovery as well as of that of intermediate thio-compounds formed by partially displacing the oxygen of the isocyanurates by sulphur.

Hofmann, in his Faraday lecture, after recalling the work Liebig did on the cyanides and cyanates, remarks: "From the cyanates there is but one step to the *sulphocyanates*," and then proceeds to say:—

"This name will recall to every chemist here, I feel assured, one of the most interesting of the many series of substances with which the indefatigable toils of Liebig have enriched our science. It would be vain to attempt anything like an encyclopædic account of the splendid chain of compounds derived from ammonium sulphocyanate: to exemplify the features of this chapter of Liebig's work, we must be satisfied to glance rapidly at one or two groups of these bodies; and I will select for this purpose, with your permission, the bases of the melamine series and the mellonides."

The interest which the pupil displayed in the same group of compounds may have been in part inspired by contemplation of the master's work; but when we consider how Hofmann's fundamental discovery of phenyl (iso)cyanate, and of the corresponding mustard oil, was gradually elaborated in the course of years, and we contemplate "the splendid chain of compounds" to which it gave rise, we cannot but feel that the work of the pupil is full worthy of being ranged with that of the master.

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Before leaving his work on sulphur compounds, reference may be made to the recognition of the oil of *Cochlearia officinalis* as

the mustard oil of the butyl series (*Ber.*, 1869, **2**, 102). To ascertain the nature of the butyl present, he prepared normal, iso- and secondary butyl mustard oils, and identified the natural oil with the last of these (*Ber.*, 1874, **7**, 508). It does not appear to have been noticed whether the natural oil is optically active as it should be.

Being struck by the remarkable resemblance of the odour of benzyl mustard oil (*Ber.*, 1868, **1**, 201) to that of watercress, Hofmann examined the oil from this and a number of other plants having similar odours. He arrived at the surprising result that the oils from *Tropæolum majus* and *Lepidium sativum* (garden cress) consist of alphetoluic nitrile, $C_6H_5 \cdot CH_2 \cdot CN$, and that of *Nasturtium officinale* (watercress) of the homologous phenylpropionic nitrile (*Ber.*, 1874, **7**, 518, 520, 1293).

A very remarkable sulphur compound of the colour of potassium bichromate, formed on mixing an alcoholic solution of strychnine with a solution of yellow ammonium sulphide, was accidentally discovered by Hofmann in 1868; he at first thought that this was a compound of strychnine with a persulphide of hydrogen of the formula H_2S_3 , but on subsequently examining it (*Ber.*, 1877, 1087) he came to the conclusion that its composition was represented by the formula $(C_{21}H_{22}N_2O_2)_2 \cdot H_2S_6$.

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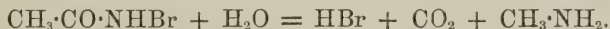
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An investigation which led to results of considerable practical importance was that on the action of bromine on amides, of which Hofmann published particulars in 1881 (*Ber.*, 2725) and 1882 (*Ber.*, 407, 752, 762).

The first product was shown to be an addition compound convertible by the action of alkali into a monobromamide, *e.g.*, acetylmonobromamide, $CH_3 \cdot CO \cdot NHBr$, in the case of acetamide. When subjected to the further action of alkali, the bromamide is converted into carbon dioxide, hydrogen bromide and the amine of the hydrocarbon radicle of the acid from which the amide is derived, thus



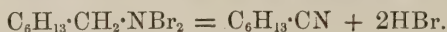
The amine, however, is but the end product, the amide being first converted into the cyanate, $CH_3 \cdot CO \cdot NHBr = HBr + CO \cdot NCH_3$. Consequently, when a mixture of two molecular proportions of acetamide with one of bromine is acted on by alkali, methylacetylurea is formed by the union of the cyanate with the excess of acetamide.

Hofmann prepared the whole series of amines up to nonylamine, as well as heptadecylamine (from stearic acid). Many interesting details with regard to the behaviour of the various amides and the products obtained from them—including a number of urea and cyanuric derivatives—will be found in the original papers; a discussion

of the best methods of preparing the amides was published at the close of the inquiry (*Ber.*, 1882, 15, 977).

The method appears to be of general application in all cases in which it is desired to withdraw carboxyl from an acid and displace it by amidogen, being the reverse of the method, also introduced by Hofmann, of converting an amine into the nitrile containing another atom of carbon by distilling its oxalate. It has already been made use of successfully in a number of cases in dealing with acids of unknown constitution. Instances in which the method is used with but partial success were described by Hofmann in 1885 (*Ber.*, 2734).

It remains to be mentioned that he also showed that the amines are themselves attacked by alkaline bromine solutions, being converted into the corresponding nitriles, and that the yield of amine is on this account often considerably below the theoretical amount; this happens more especially in the case of the higher terms of the series, as little as 30 per cent. of the theoretically possible amount of heptylamine being obtained, although as much as about 70 per cent. of hexylamine is produced. The formation of the nitrile is due to the conversion of the primary amine into the dibromamine, which then loses two molecular proportions of hydrogen bromide, *e.g.*,



As Hofmann aptly remarks, the operation may be regarded as a reversal of Mendius's well known process of converting the nitriles into amines (*Ber.*, 1883, 558; 1884, 1406, 1920), and, as he showed, it may be used as a method of gradually passing down just as Mendius's process has been used in passing up the series.

* * * * *

Dr. Perkin has drawn attention, in his account of Hofmann's work on colouring matters and allied subjects, to Bardy's method of preparing the methylanilines by heating aniline hydrochloride with methyl alcohol under pressure.

In studying this method, Hofmann and Martius were led to make the important discovery that when the action was allowed to take place at a high temperature, methylated homologues of aniline were also formed; in fact, by using an excess of alcohol and heating at 280—300°, they obtained a complete series of methylated derivatives up to the tetramethylated compound, $\text{C}_6\text{H}(\text{CH}_3)_4\text{N}(\text{CH}_3)_2$, (*Ber.*, 1871, 4, 742).

We can have no doubt who wrote the account of the work, when we read

“Wir vermissen mit Schmerzen das letzte Glied dieser Reihe, die Base mit *pentamethylirter* Phenylgruppe; wir haben sie aber trotz mehrfacher Anläufe nicht bis jetzt fassen können.”

But in course of time Hofmann's grief was assuaged, as he was able to show that not only the pentamethylated base but also hexamethylbenzene were among the products when the methylating process was prolonged (*Ber.*, 1872, 720; 1882, 2895; 1884, 1912; 1885, 1821). In carrying out his later researches he had at his disposition material obtained in manufacturing solid cumidine—1 : 2 : 4 : 5-amido-trimethylbenzene—on the large scale from xylidine by the process which Martius and he had discovered (*Ber.*, 1876, 1292, 1299).

In their first paper, Hofmann and Martius had dealt only with the products which were volatile with steam; in a later paper they gave an account of the non-volatile products, especially of a tertiary diamine, $C_{15}H_{14}(NMe_2)_2$ (*Ber.*, 1873, 345; and they had meanwhile examined amidoethylbenzene, in order to compare it with the products they obtained from aniline (*Ber.*, 1869, 412).

To gain an insight into the nature of the changes involved in the methylating process, Hofmann studied the behaviour of trimethylphenylammonium iodide and showed that the methyl groups "wandered" one by one into the phenyl, giving rise finally to an amido-trimethylbenzene (*Proc. Roy. Soc.*, 1872, **21**, 47) which he subsequently identified with mesidine (*Ber.*, 1875, 61). The process was found to be equally applicable to secondary and tertiary salts, and also to the production of ethyl and amyl, but not of phenyl derivatives, diphenylamine hydrochloride remaining unchanged. Tetramethylammonium iodide was also found to be unaffected.

With regard to the position which the groups take up in the benzene nucleus, it is noteworthy that whereas Hofmann obtained paratoluidine on heating methylaniline hydrochloride, the hydriodide gave a liquid toluidine—doubtless the ortho-compound; phenyltrimethylammonium iodide, it should be added, afforded two dimethyltoluidines.

Some uncertainty attaches to Hofmann's results, in so far as the origin of the various products he obtained and their genetic relationship with aniline is concerned, as later researches by Limpach (*Ber.*, 1888, **21**, 640) appear to show that the methylation follows the ordinary para-ortho-law, and that although the presence of methyl in the meta-position in no way retards the action, methyl cannot be directly introduced into a meta-position by Hofmann's method. If this be the case it would seem, therefore, that the tetramethylated compound obtained originally by Hofmann and Martius must have been derived from xylidine present in the aniline used; and that the pentamethylated compound which the former prepared from commercial cumidine—derived from a mixture of xylidines—must have had a somewhat similar origin. It is, in fact, difficult on reading Hofmann's accounts of the investigation to ascertain to what extent the technical

products used in preparing the materials he examined were definite substances.

Further evidence pointing to the same conclusion is afforded by his remarkable observation that the dimethylxylidine prepared from trimethylphenylammonium iodide—1 : 2 : 4-xylidine—combines with methyl iodide with remarkable slowness, even at 150°, and that the trimethylated base from the same source—mesidine, as well as the tetra- and penta-methylated bases prepared from solid 1 : 2 : 4 : 5-cumidine, cannot be caused to combine with the iodide. Yet Martius and he prepared methiodides from the entire series of methylated anilines they obtained in their original investigation, and inability to form methiodides cannot therefore be regarded as a property of all the higher methylated anilines.

Hofmann appears to have been of opinion that, in the first instance, the hydrogen chloride of the aniline salt gives rise to the formation of methyl chloride, which in its turn, as he expresses it, induces substitution, first in the ammonia fragment, and ultimately in the phenyl group itself, the essential character of the process being an intramolecular change in the position of the methyl groups. Subsequently, in discussing the formation of hexamethylbenzene (*Ber.*, 1880, **13**, 1729), he suggested that the aniline underwent conversion into benzene and ammonia under the influence of the methyl alcohol, which itself became methaldehyde in the process, and that the nascent benzene was acted on by the methyl chloride and methylated.

Bearing in mind that in his original investigation on the amines he had shown that the secondary and tertiary amines are readily reconverted into primary amines by heating their hydrochlorides (*Proc. Roy. Soc.*, 1860, **10**, 594), it appears doubtful whether the process is one of direct intramolecular change; it is more probable that methylation is the result of the direct addition to the hydrocarbon radicle of the aniline of the methyl chloride or iodide, or other similar compound, and the subsequent separation of hydrogen chloride or iodide under the influence of the base present. Michel, in fact, long ago advocated this explanation (*Ber.*, 1881, **14**, 2107).

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But one series of investigations carried out by Hofmann in Berlin remains to be considered—that relating to piperidine and conine, commencing in 1879, in the course of which he devised the method of removing the nitrogen from such compounds now recognised as one of the most important means of deciphering the constitution of alkaloids.

It seems strange to read that at so recent a date the constitution of piperidine was still undetermined, and that, although recognised to

be a secondary amine, the nature of the group C_5H_{10} , combined with NH was entirely unknown; in the hope of dissecting out the constituents of this group, Hofmann strongly heated the hydrochloride of the base, but to no purpose. He then heated it with bromine, and obtained a product, $C_5H_2Br_2(OH)N$, which appeared to be a derivative of pyridine, but this, on similar treatment, gave only a dibromo-derivative (*Ber.*, 1879, **12**, 984).

Königs soon afterwards showed that piperidine and pyridine were related in the manner suspected by Hofmann, by oxidising the former with concentrated sulphuric acid and so converting it into the latter (*Ber.*, 1879, 2341); and Schotten subsequently obtained a dibromopyridine from piperidine identical with that prepared by Hofmann from pyridine (*Ber.*, 1882, **15**, 427). Finally, Hofmann himself obtained pyridine by subjecting acetyridine to the action of bromine (*Ber.*, 1883, **16**, 586).

Turning his attention to conine, he showed that this alkaloid contained two more atoms of hydrogen than had previously been supposed (*Ber.*, 1881, **14**, 705); and at a much later date, having distilled its hydrochloride with zinc dust, in the hope of converting it into octylamine, he obtained conyryne, $C_8H_{11}N = C_8H_{17}N - 6H$, and proved that this was either propyl or isopropylpyridine, and conine the corresponding piperidine derivative, by oxidising it to picolinic or pyridine-orthocarboxylic acid. He reconverted conyryne into conine by means of hydrogen iodide. The relation of conine to pyridine, which had often been suspected, was thus placed beyond doubt (*Ber.*, 1884, **17**, 825).

Having failed to obtain any information as to the constitution of the hydrocarbon group in piperidine by means of the experiments above referred to, recalling to mind his old observations on the decomposition of the ammonium hydroxides by heat, Hofmann subjected dimethylpiperidylammonium hydroxide to distillation. The result was an entirely unexpected one, as the hydroxide was resolved into water and "dimethylpiperidine," a compound which Hofmann regarded as formed by the passage of a methyl group into the hydrocarbon radicle. However, on combining the compound thus produced with methyl iodide, and distilling the corresponding hydroxide, trimethylamine and an unsaturated hydrocarbon, C_5H_8 , were obtained (*Ber.*, 1881, 494, 659).

Conine behaved in a precisely similar manner, giving "dimethylconine," and ultimately trimethylamine and conylene, C_8H_{14} , a hydrocarbon which had been prepared from nitrosoconine by Wertheimer many years before (*Ber.*, 1881, 705).

Having ascertained that conine had the formula $C_8H_{17}N$, Hofmann was led to examine *conydrine*, a substance occurring together with

conine in hemlock, as Wertheimer—who had assigned the formula $C_8H_{17}NO$ to this base—had stated that it could be converted into conine by dehydrating agents. Hofmann confirmed Wertheimer's formula for conydrine, but on subjecting this substance to the action of muriatic acid at 220° , he obtained two isomeric bases of the formula $C_8H_{15}N$ —liquid α -coniceïne and solid β -coniceïne (*Ber.*, 1881, 14, 1497; 1884, 17, 1908). A third substance of the same composition, γ -coniceïne, was obtained on subjecting conine to the action of bromine and alkali. It was shown that α -coniceïne could also be obtained from conine, and that conydrine was convertible into conine (*Ber.*, 1882, 15, 2313; 1885, 5, 109).

The remarkable results arrived at in the case of piperidine and conine naturally led Hofmann to study the effect of heat on pyridine ammonium derivatives. The results were altogether different, however, from those obtained in the case of the reduced pyridines, mono-substituted hydro-bases being formed, *e.g.*, methylhydropyridine, $C_5H_5N(CH_3)H$. The substances thus produced are characterised by their unpleasant odour, resembling that of the isonitriles and mustard oils, and on this account it was suggested by him that their production might be made use of as a means of recognising pyridine bases. The action which gives rise to them is of a very complex nature, and the yield exceedingly bad; in the hope of devising a more satisfactory method of preparation, he subjected the pyridyl ammonium iodides to the action of sodium amalgam, but obtained what appear to be dipyridyl compounds.

In studying the action of bromine in presence of alkali on the amides of polybasic acids—a series of experiments which afforded only negative results—Hofmann, in conjunction with Behrmann (*Ber.*, 1884, 2681), had occasion to examine citramide and the citraminic acids, and in the course of the inquiry was led to the discovery of citrazinic acid, a pyridine derivative from which Sell and Easterfield have but recently prepared a number of derivatives of exceptional interest.

* * * * *

Everyone is acquainted with Hofmann's modification of Gay Lussac's classical method of determining vapour density by volatilising a known weight of substance and determining the volume of vapour at a known temperature and pressure. His use of the barometric vacuum for the purpose (*Ber.*, 1868, 1, 198) has the great advantage, not only of being an exact method, but also of permitting of the determination of vapour density at temperatures considerably below the boiling point of a substance under atmospheric pressure. A variety of improvements of minor details were described by him in

1876 (*Ber.*, 9, 1304); and other communications on the determination of vapour density, which he brought under notice in 1877 (*Ber.*, 10, 962) and 1878 (*Ber.*, 11, 1684), show that the subject continued to engage his attention. It should not be forgotten that in introducing his method, Hofmann also introduced the system of using the vapour from a boiling liquid to heat the tube; although not new in principle, this was a most important practical step in advance.

* * * * *

No notice of Hofmann's scientific work would be complete if reference were not made in it to the remarkable service he rendered as a teacher in the lecture room. Sir F. Abel and Dr. Perkin have both spoken of the attention he lavished on experimental illustrations, and all who have heard him lecture are aware of the remarkable enthusiasm he invariably displayed over every successful demonstration his assistant was able to perform—for he was not often allowed by his assistants to perform his own experiments, however much they were of his own devising.

But Hofmann did not merely devise new experiments—as he tells us in the preface to his *Modern Chemistry*, in endeavouring to promote, in the country of his adoption, *the great cause of chemical education*, he broke with the classical traditions of chemical teaching; and besides studying the elements in a new order, introduced an altogether new style into lecture experimenting. This was done in response to a deeply felt want, due to his conversion to “Gerhardtism;” in fact, he commences the discourse “On Lecture Illustrations” he delivered to our Society in February 1865 by saying—

“The introduction into modern chemistry of the idea of structural types, and the prominence given thereby to volumetric considerations, involve the necessity of modifying, to a certain extent, our present style of lecture illustrations. This necessity, I believe, has been felt by many teachers who have endeavoured to reflect the present aspect of chemistry in their lectures.”

He gave an account, on the occasion in question, “of the volumetric experiments on the composition of the typical hydrogen compounds” with the study of which, during the previous few years, he had been in the habit of opening his course of lectures on experimental chemistry. The well known experiments on the volumetric composition of hydrogen chloride, water, ammonia and methane were then brought under notice. The account of the lecture printed in our Journal is illustrated with figures of the volumetric apparatus now so familiar to all students of chemistry, taken from his *Introduction to Modern Chemistry, Experimental and Theoretical: Lectures delivered in the Royal College of Chemistry, London*, which was published shortly afterwards.

He delivered a second discourse on lecture experiments on an

especially auspicious occasion, on May 15, 1869, when the German Chemical Society, of which he was President, at his invitation, met in his new laboratory in Berlin, completed only a week before.* The lecture was prefaced by an account of the steps that had led to his appointment and to the building of the laboratory, commenced on May 15, 1865. In the course of this address, referring to the opening of large chemical laboratories at Berlin and Bonn, both erected under his direction, he gave utterance to the following forecast—

“Man wird sich nicht täuschen wenn man der Gründung der beiden gross-

* The experiments brought under notice in his lecture had reference to—(1) Increase in weight during combustion; (2) Formation of ferric acid; (3) Volumetric analysis of muriatic acid and ammonia by electrolysis; (4) Condensation of hydrogen and oxygen on conversion into gaseous water; (5) Analysis of methane and ethylene; (6) Lecture eudiometer; (7) Equality of volume between oxygen and the carbon and sulphur dioxide into which it is converted; (8) Oxidation of ammonia; (9) Evolution of oxygen from nitric and sulphuric acids; (10) Flame experiments; (11) Lecture thermoscope; (12) Comparison of the volumes of different gases when subjected to the same alterations of temperature and pressure; (13) Compression of gases by mercury; (14) Liquid sulphur dioxide; (15) Production of mercury bubbles on water; (16) Local ventilation for lecture experiments (*Ber.*, 1869, 223).

Experiments on the following subjects were afterwards described in the *Berichte* —(17) Combustion phenomena (1869, 4371); (18) Inflammation of hydrogen compounds in contact with nitric acid; (19) Observation of complementary colours in transmitted and reflected light; (20) Colouring power of aniline dyes; (21) Formation of nitric acid on combustion of hydrogen in air; (22) Liquid cyanogen; (23) Alternate reduction and oxidation (1870, 658); (24) Preparation of pure phosphine; (25) Decomposition of phosphine by electric sparks (1871, 200); (26) Eudiometer with movable sparking wires; (27) Doubling of volume on conversion of carbon dioxide into monoxide by carbon (1871, 243); (28) Oxidising action of carbon; (29) Demonstration of oxidation by conversion of colourless into coloured compounds; (30) Liquid phosphine; (31) Maximum density of water; (32) Sodium press; (33) Reversed Lidenfrost experiment to show behaviour of alkali metals to water (1874, 530); (34) Volumetric equivalence of oxygen and chlorine; (35) Analysis of hydrogen chloride; (36) Formation of water on a large scale; (37) Demonstration that gases may be liquefied both by pressure and cold (1119); (38) Electrolysis of muriatic acid; (39) Volumetric phenomena attending the formation of hydrogen chloride from hydrogen and chlorine; (40) Combustion phenomena; (41) Equality of volume of carbon dioxide with that of the oxygen from which it is formed; (42) Combustion of oxygen in hydrogen; (43) Volume weight of gaseous water; (44) Volumetric relationship of liquid and gaseous water; (45) Maximum density of water; (46) Decomposition of water by sodium; (47) Alternate decomposition and formation of water; (48) Volumetric analysis of ammonia; (49) Volumetric relation of ammonia to the nitrogen it contains; (50) Liquefied gases; (51) Manufacture of sulphuric acid; (52) Demonstration of Dulong and Petits' law; (53) Equivalence of lead and zinc; (54) Reversed Lidenfrost experiment (1882, 2656).

artigen chemischen Laboratorien, welche sich in diesem Augenblicke unter den Auspicien der Königlichen Unterrichts-Ministeriums vollendet haben, eine Bedeutung beilegt, die weit über den unmittelbaren Nutzen für den Aufschwung des chemischen Unterrichts auf den betreffenden Universitäten hinausgeht. In der Bewilligung der ausserordentlichen Mittel für die Organisation der neuen Institute ist dem Einflusse der Chemie auf die Entfaltung moderner Zustände eine Anerkennung gezollt worden, welche nicht ohne Einwirkung auf die übrigen, an diesen Errungenschaften kaum weniger beteiligten Naturwissenschaften bleiben kaum. Den eben entstandenen chemischen Instituten werden sich ähnliche, mit gleicher Liberalität ausgestaltete Anstalten für die beiden anderen grossen Zweige der Naturwissenschaft, Physik und Physiologie, anreihen, denen neben der Chemie die Zukunft angehört. Schon regt es sich lebhaft in diesem Sinne. Die Vertreter aller naturwissenschaftlichen Disciplinen fühlen, dass die grossen Opfer, welche man noch eben einem einzigen Zweige der Naturwissenschaft gebracht hat früher oder später dem eigenen Fach zu Gute kommen müssen."

Events, in his own country, have abundantly justified these remarks. Of the use made of the laboratory under his direction, evidence is to be found in the pages of the *Berichte*; all know that extraordinary activity prevailed in it, and some indication of the extent to which it was used is afforded by the fact that the last communication bearing his name, published in 1892, is marked

"Aus dem I, Berliner Univ.-Laborat, No. DCCCLXXXVIII."

Although Hofmann was not the first to study the effect of electric sparks on compound gases, the form in which we have long been accustomed to make such experiments is mainly of his devising, and had its origin in a series of remarkably interesting observations which Buff and he described in a communication to our Society in 1859 (*Chem. Soc. J.*, **12**, 273). Their experiments were undertaken

"in the hope that the slow decomposition of compound gases by the long continued passage of electric sparks might be effected by the spark current of the induction coil with such rapidity and precision as to furnish a simple experimental illustration of relations with difficulty attainable by other methods. The relation of the spaces occupied respectively by a compound gas and by the sum of its gaseous constituents is but rarely capable of *synthetical* demonstration. In most cases this relation can only be exhibited by *analytical* operations which are not always compatible with the conditions of a lecture experiment. The successful application of the spark-current appeared to promise a considerable simplification of these processes. With this view we have studied the action of the current produced by a powerful Ruhmkorff coil on the more frequently occurring compound gases and on the vapours of several liquids of low boiling point. At the same time we examined the deportment of these gases and vapours under the influence of iron or platinum coils electrically incandescent, together with the effects produced by the high temperature of the electric arc."

Among the substances sparked was carbon dioxide: they observed that this was at first decomposed into carbon monoxide and oxygen, which, after a time, recombined explosively. Thirty years later, almost at the very close of his career, Hofmann was led again to pay attention to this subject by representations from others that they had not succeeded in verifying the statement. He went fully into the matter, and showed under what conditions the alternations in the phenomena could be observed (*Ber.*, 1890, **23**, 3303). Both communications are full of interest, both on account of the observations recorded in them and of the practical information they convey; it is remarkable that the ingenious method of sparking introduced by Buff and Hofmann has not been more frequently adopted by later workers.

* * * * *

The foregoing is an account, in the briefest possible terms, of the scientific work accomplished by Hofmann during a period of almost 50 years—of labours ever carried on with unremitting ardour and enthusiasm, no trace of failing interest being discoverable as years roll on, the same characteristic, inspiring freshness of style pervading each successive communication.

Much may be learnt by the reverent study of his work; and this notice has been compiled in the hope that it may, in some measure, serve students as a guide—to enable them to grasp its bearings, and to understand the intimate interconnection of its parts.

No more enduring monument of his supreme ability as an investigator could be wished for than is afforded by the records of his labours preserved to us in the various journals. And not only of his ability as an investigator—for in studying them we perforce recognise the great leader also. No ordinary man could have induced his assistants so rapidly to carry out researches of such difficulty as that on the diamines, and so repellent as well as difficult as were those on the phosphines, the isonitriles, the isocyanates and the mustard oils.

But we cease to wonder, when we learn how closely he followed each step in every investigation which was being carried out under his direction, how every detail even was familiar to him; and when we hear how all who worked with him were stirred into enthusiasm, and were made to feel that failure to produce results was regarded by him as a real personal grievance.

Hofmann, however, not only provided most of the materials for one of the chief chapters in organic chemistry—he played besides the part of the statesman, and with marvellous effect; for the great



A. W. v. Napmann

work accomplished under his leadership by the German Chemical Society—which has coordinated the labours of chemists throughout the world in a way that has never yet been witnessed in any other branch of science—is universally recognised as largely due to his initiative, to his great organising ability, and to his personal exertions, influence and tact. We are able to take no small share of pride in his success, as he was the first to recognise that he gained his experience among us, and that he was often guided by English models.

Cosmopolitan in speech, he was cosmopolitan in sympathies. A discovery of interest once made in his English laboratory, he forthwith communicated his results not only either to us or to the Royal Society and to his former countrymen, but also to his many friends and admirers in France; and he would have been equally ready to give expression to them in several other tongues had he felt that any useful purpose was to be served. It was no mere vain wish for notoriety that led him to spread abroad the account of his successes. The interest he took in his work was so intense, that he could not but feel that others ought to be able to enjoy with him the pleasure he experienced whenever new facts of importance came to light. Hofmann's share in promoting the spirit of freemasonry among scientific workers generally was thus very great.

And his influence in industrial circles cannot well be overrated, difficult though it be to gauge its extent. Apart from the inspiration men like Perkin and Nicholson received from him, there can be no doubt that his researches on colouring matters have had a determining effect on the course of the development of the colour industry. Had it not been for the example which he set, and the persistent manner in which he investigated colour after colour, problem after problem, we should scarcely have so soon witnessed that translation of theory into practice which is the distinguishing feature of *German chemical industry* at the present day.

It would be impossible to find a more competent witness than the author of the epic—for it is nothing less—published shortly after Hofmann's death in the *Berichte*, recounting the wondrous achievements of the long succession of chemists who have brought the coal tar industry to its present high pitch of perfection; in claiming for Hofmann a principal share in its development, Caro indulges in no mere flight of poetic phantasy, and the following closing words of his recital are singularly appropriate and full of feeling—

“Dem Führer folgen wir zu dem Fabrikthor. Noch einen letzten Blick in die Gliederung des mächtigen Werkes—sein wahres Fabrikgeheimniss wurde uns offenbart!

“Vor unserm Geiste steht wieder der Baum der Deutschen Chemischen

Industrie mit seinen ragenden Aesten und Zweigen. Wie naturgemäss—denken wir—hat sich doch sein kräftiges Wachsthum vollzogen! Boden und Nahrung fand er in der Wissenschaft und das Walten der ewigen Gesetze, die jeden Erfolg im Leben bedingen, hat auch seine Entwicklung zu der gegenwärtigen Blüthe gebracht. Der Wunsch ringt sich von der Seele los—Möge nie der Sturm diesen Baum entblättern, nie der Unfriede an seinem Marke nagen!

“Wir sagen dies dem Führer. Er drückt uns die Hand. ‘Und so oft Sie sich dieses Baumes erinnern, so vergessen Sie nicht’—sagt er—des treuen Gärtners, der unseres Zweiges gewartet hat, seit der Zweig noch ein Reis war—fast ein halbes Jahrhundert. Denken Sie stets in Liebe und Verehrung an unsern August Wilhelm von Hofmann.”

Hofmann did his best to raise up an English tree of chemical industry, and for a while it grew apace: indeed, at one time there seemed to be every chance that it would rank as an indigenous production, as seed fell and began to spring up in turn; but alas! its roots were soon struck by canker, and it ceased to flourish. No one could be brought to understand that it not only required frequent careful pruning, but also the addition continually of new grafts; it was left too much in the charge of mere uninstructed labourers, and competent foresters who could appreciate its requirements and forward its growth were considered unnecessary.

While our adopted countryman, Hofmann strove in every possible way to promote our interests. His pupils established the new industry, which he did his utmost to support and forward when its importance once became manifest; but the circle within which favourable conditions prevailed was hopelessly narrow. We, in fact, denied him the opportunity he eagerly seized upon when it was offered to him by his own countrymen: and among them he found both *Boden und Nahrung*, for they had been properly tutored by their universities, and were prepared to accept his advice and *apply theory to practice*. Our universities, unfortunately, long thwarted us instead of aiding us, and are still too much engaged in the blind worship of the unpractical. True culture has been neglected. The struggle for scholarships and distinctions has exercised an over-mastering influence; precious years which should be spent in learning to *work* and to appreciate and apply theory have been sacrificed in committing facts to memory for the mere purpose of retailing them in examination halls—nay, worse, in sterilising and cramping minds which under a free system might develop into utmost usefulness. A change is indeed gradually coming about, but all too slowly, as—worst of all—no true public feeling on the question exists. Our schools have done their work so badly that the general public cannot properly discuss such questions, and take no interest in them.

The records of our Society show what English chemists can accom-

plish, and if the demand should arise there would now be no difficulty in finding and educating any number of capable men who could do all that would be required of them. But so long as employers of labour are not thoroughly imbued with the scientific spirit, and fail to fully avail themselves of the services of properly trained workers, no real progress is possible: for it is useless to manufacture goods you cannot sell to advantage, which those who ought to possess them will not buy.

Those of us who understand the position cannot but contemplate with envy, and yet with utmost admiration, proud words such as Caro utters in referring to the coal tar industry: "Kein Zweig der deutschen Technik trägt mit gleichem Rechte den Namen einer nationalen Industrie." It were time, however, that some sense of shame pervaded our men of business, and that the nation were brought to understand how opportunities once ours have been sacrificed, not even blindly, but in face of constant warnings; that not only the coal tar industry, but all industries in which chemistry can and should play the leading part, with few exceptions, have failed to advance during the past five and twenty years.

To quote the words used by the Council of the Royal College of Chemistry in their second report in 1848—"Capital, which has been the boast of this country, can do much, but capital directed by the lights of science may accomplish much more; and those nations who neglect to call in its aid, will, to use the prophetic words of the venerable *Humboldt*, infallibly see their prosperity diminish in proportion as neighbouring countries become strengthened and invigorated under the general influence of arts and science." It were time that the value of the legacy Hofmann has left were appraised by us—that some notice were taken of the warning which at the outset of his English career he brought under our notice.

A writer in a recent number of the *North American Review* maintains the thesis that chemistry underlies the manufacturing arts, and that hence the industrial status of a nation may be fairly estimated by the condition of its chemical knowledge.

"It is fair to hold that the country that has the best chemists will in the long run be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best manufactured materials, the fewest wastes and unutilised forms of matters, the best guns, the strongest explosives, the most resistant armour. Its inhabitants will make the best use of their country's resources; they will be the most healthy, the most free from disease; they will oppose the least resistance to favourable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition to-day between nations is essentially a competition in the science and applications of chemistry."

Hofmann consistently taught this doctrine when he came among us—but to no purpose; his countrymen were wiser and have proved its truth to demonstration, and the victories won in the fields of pure and applied chemistry are rapidly leading them to introduce scientific method into the conduct of their affairs generally.

Shall we ever decline to pay heed to one whom we always admired and whom we now venerate?

Hofmann was elected a Foreign Member of the Chemical Society on March 3rd, 1845, which is in itself proof of the esteem in which he was held within two years after the publication of his first paper.

He became an ordinary member of the Society in 1849, the record of the meeting on March 3 containing the entry "Augustus W. Hofmann was elected a Member of the Society."

Meanwhile he had already been appointed Foreign Secretary (in 1847); and he held this office until 1861, when he was elected President.

The Society became of age during his first year of office as President, and in this year also the Prince Consort died, who had taken so great an interest in his work and in the Royal College of Chemistry. In his second year of office, the Great Exhibition was held, with which his name will always be connected on account of the remarkable monograph he wrote describing the chemical exhibits.

As Vice-President he retained his position on our Council and as an ordinary member of the Society during the remainder of his life; but after leaving England he took no part in our work, and only once came to a meeting. Although he communicated several of his discoveries to the Royal Society, he did not once send a paper to us.

He delivered the Faraday lecture in 1875, selecting as his subject Liebig's work.

His last appearance among us was in 1884, when he presided at the dinner given on the 23rd of April in honour of his old pupil, Perkin.

He was elected a Fellow of the Royal Society in 1851. He received the Royal Medal in 1854, and the Copley Medal in 1875.

Hofmann died suddenly at Berlin, on May 5, 1892, in his 74th year.

Of the two portraits attached to these notices, one is from a photograph of Hofmann taken shortly before he left England, the other is from the heliogravure of the portrait now in the Berlin Gallery, painted in 1890 by Angeli, the celebrated German artist.

OBITUARY NOTICES.

S. W. M. DAVY, who was born at Fallowfield, near Manchester, on November 9, 1861, commenced his education at a private school, and at the early age of nine gained a Scholarship at the Manchester Grammar School, where he remained seven years; during this time he took great interest in chemistry, experimenting at home in his spare time in a room given up to his use for that purpose. After leaving the Grammar School, he was apprenticed to Mr. C. Estcourt, city analyst, Manchester, and being very friendly with Dr. Burchardt, of Owens College, was permitted to attend his private lectures, and received much kindness from him. At the expiration of his apprenticeship he was placed for three years with Mr. Bird, of South Down, assayer and owner of chemical works, near Plymouth. After leaving South Down he was appointed Analyst to the Manchester Corporation Gasworks, where he remained five years under the late Dr. John Leigh; from there he went to the Sheffield Gasworks as analyst and chemist, a position he held up to the time of his death. He was not only fond of the science which was his profession, but devoted many spare hours to painting, both in oil and water-colours, leaving behind him many mementoes of his skill in this art.

ROBERT GALLOWAY, the second son of Robert Galloway, was born on January 9, 1822, at Cartmel, Lancashire, and was educated at the Grammar School there; at a very early age he evinced a taste for the science which afterwards became his profession. On leaving school, he went as an assistant to Mr. Ross, chemist, of Lancaster, in whose establishment he met as a colleague, Edward Frankland, who has since become so distinguished as a chemist. He then proceeded to London, to study at the College of Chemistry under Dr. Hofmann, and after a time accepted the post of Teacher of Chemistry, at Queenwood College, Hants, as successor to Frankland and Tyndal. He then became assistant to Dr. Lyon (now Lord) Playfair, who subsequently recommended him for the position of Professor of Applied Chemistry, at the Museum of Irish Industry at Dublin. At that institution, which afterwards became the Royal College of Science for Ireland, he continued to hold for many years the chairs of theoretical and practical chemistry and of metallurgy, until he retired on full pension in 1880.

He was pre-eminently a teacher and practical man, and devoted his energies to his pupils rather than to his own original work. Many of those who received their early training in chemistry from him

have since attained to eminence in chemistry, in the industrial arts, and in the learned professions. His writings were numerous, voluminous, and important, and in addition to papers on industrial chemistry presented to the Royal Irish Academy, published in the *Chemical News*, and in pamphlet form, &c., the following may be particularly noted:—*A Manual of Qualitative Analysis* (1850), of which five editions have since been called for; *The First Step in Chemistry* (1851), which also has passed through many editions, and which long maintained its place as the best elementary text-book on the subject; *The Second Step in Chemistry* (1863), a singularly able and comprehensive compilation of advanced work in chemistry; *A Treatise on Fuel* (1880); *Education: Scientific and Technical* (Trübner, 1881); and *The Fundamental Principles of Chemistry* (Longmans, 1888). He died in London, on January 15, 1896, aged 74.

Robert Galloway is remembered by his pupils with affection and respect, for his unsparing trouble as a teacher, his kindly interest and encouragement in their subsequent careers, and his high character as a man of science. He would brook nothing that he considered unthorough, and if he made enemies, it was on account of his outspoken condemnation of everything that he regarded as disingenuous or untruthful.

GEORGE M'ROBERTS was born 56 years ago, and commenced his business career in the office of Russell and Sons, coalmasters, Falkirk. He afterwards took up the profession of chemistry, in which he occupied a high position. He was well known as the founder of the Westquarter Chemical Works, Redding, and on obtaining the appointment of Manager of Nobel's Explosive Works, Ardeer, he sold his works at Redding to Nobel's Explosives Company, who extended them and carried them on as a branch of their large undertaking. While at Ardeer, Mr. M'Roberts made the first charge of dynamite used in this country. Latterly he was employed as Technical Adviser to the British Explosives Syndicate at Pitsee, Essex. Mr. M'Roberts was very popular in Ardeer and that district, and was held in high esteem by the employés of the works, and by all with whom he came into contact. He retained his connection with the works at Ardeer until eight years ago, when, owing to the delicate state of his health, he was compelled to retire; he then took up his residence at Newton Mearns, where the last years of a busy life were spent in comparative retirement. Mr. M'Roberts was well known in Falkirk and the neighbourhood, and was held in high esteem by all who had the privilege of his acquaintance; he was a Justice of the Peace for the county of Ayr. He was married to

a daughter of the late Mr. Paton, of Thornbank, Falkirk, for whom much and sincere sympathy is felt in her sad bereavement. Mr. M'Roberts had been in delicate health for the last eight years, but his death took place somewhat suddenly at his residence, Todhill, Newton Mearns, from an affection of the heart.

HENRY DAVIS POCHIN, who died at Bodnant Hall, Denbighshire, in his 72nd year, on October 28th, 1895, after a short illness, was for many years a prominent and widely known figure in English commercial life, and illustrated by many examples the successful application of scientific discovery to practical purposes. He studied chemistry in early life, with the view of entering business in Manchester as a Manufacturing Chemist, and by experimental research, which resulted in the patenting of many valuable inventions, he built up the firm of H. D. Pochin & Co., in Salford. Through his process for decomposing silicate of alumina, the article known as "aluminous cake" was introduced into commerce, and is now extensively used by paper-makers, whilst his discovery of the method of distilling resin with superheated steam forms the basis of the modern manufacture of a certain class of yellow and fancy soaps. About 30 years ago, in combination with a few business friends, he acquired some of the principal coal, iron, and steel concerns in the country; and although he converted them into limited liability companies he retained the largest interest in the capital, and the chief part of the direction in his own hands. In this way he became known as the leading spirit in Bolckow, Vaughan, & Co.; John Brown & Co.; the Armour Plate Makers of Sheffield; the Tredegar Iron and Coal Company; Palmer's Shipbuilding and Iron Company; the Staveley Coal and Iron Company; the Sheepbridge Coal and Iron Company, and other undertakings of a similar character. About the same period he took up, in conjunction with Sir Edward Watkin, the affairs of the Metropolitan Railway Company, which were then in a state of insolvency, and as Deputy-Chairman, an office which he continued to hold until his death, took a large share in creating its present condition of prosperity. He was also a Director of the Manchester, Sheffield, and Lincolnshire Railway, and for many years took an active part in connection with popular education in Manchester and Salford, and was twice Mayor of the latter borough. He was a well-known member of the Reform Club, and sat for a short time in the Parliament of 1868. In the election of 1865 he was an unsuccessful candidate for Stafford; and again, in 1874, he stood both for Stafford and Monmouth, but failed to get elected.

XLIII.—*Condensation of Benzil with Ethylic Acetoacetate.*

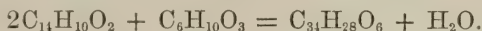
By FRANCIS R. JAPP, F.R.S., and G. DRUCE LANDER, B.Sc.(Lond.).

THE following investigation was undertaken in the hope of throwing light on the constitution of the compounds obtained by the condensation of benzil with acetone, especially on that of anhydracetonebenzil. This hope has not been fulfilled; but as we believe that we have in the meantime attained our object by the more direct method of a detailed study of the reactions of anhydracetonebenzil itself, we do not intend to carry our examination of the present condensation further, especially as, owing to the high molecular weight of the compounds formed, and the consequent uncertainty in interpreting the analytical data, the work is of great difficulty. We therefore content ourselves with placing on record the results obtained.

Action of Sodium Ethoxide on a Mixture of Benzil and Ethylic Acetoacetate.—Eight grams of sodium were dissolved in about 100 grams of absolute alcohol; the solution was cooled; 40 grams of ethylic acetoacetate and 70 grams of benzil were added; and the whole was warmed on the water bath until the benzil had dissolved, after which the flask was removed from the water bath, and allowed to stand over night. A crystalline substance was deposited, which proved to be a sodium compound of the new condensation product, and contained alcohol of crystallisation; it had the formula $C_{34}H_{27}NaO_6, C_2H_6O$. This substance was separated by filtration, and washed with cold alcohol. Addition of alcohol to the mother liquor produced a further deposit of the substance; this was treated in the same way. The second mother liquor thus obtained gave, on dilution with water, a third portion of the substance in a less pure condition.

This sodium compound, like the metallic derivatives of ethylic acetoacetate, is readily soluble in benzene. The first two crops of crystals were therefore united and dissolved in benzene, after which glacial acetic acid was added until the liquid showed a slight acid reaction. Sodium acetate separated, and was removed by filtration. The clear solution was diluted with light petroleum; on standing, the liquid very slowly deposited nearly the whole of the new compound in crystalline crusts. The yield was 42 grams, whilst a further quantity was obtained from the third crop of sodium compound. Thus purified, it contains benzene of crystallisation, and the crystals effloresce on exposure to air. It may be purified by recrystallisation, either from hot alcohol or from a mixture of ethylic acetate and light petroleum; both solvents deposit it in colourless, flat needles or

prisms, with bevelled edges. It melts with decomposition at 210—211°. It has the formula $C_{34}H_{28}O_6$, and is formed from benzil and ethylic acetoacetate, according to the equation



It may, therefore, be provisionally named *ethylic anhydrodibenzilacetate*. Analysis of the air-dried substance gave results agreeing with the foregoing formula.

0.1693 gave 0.4760 CO_2 and 0.0824 H_2O . C = 76.68; H = 5.40.

0.1973 „ 0.5534 CO_2 „ 0.0965 H_2O . C = 76.50; H = 5.43.

$C_{34}H_{28}O_6$ requires C = 76.69; H = 5.26 per cent.

The substance is somewhat difficult to burn; but we were led unnecessarily to doubt the accuracy of some of our first combustions by noticing the formation of a permanent black deposit in the combustion tube above the oxide of copper just in the neighbourhood of the substance. This we at first took to be unburnt carbon; but it proved to be oxide of copper. The phenomenon was doubtless due to the regeneration of ethylic acetoacetate, and the formation of its volatil copper compound, which was then decomposed in contact with the hotter portions of the tube. The formation and volatilisation of ethylic cupracetoacetate under such conditions may be readily shown, as we found, by heating in a test-tube a little finely powdered copper oxide, moistened with ethylic acetoacetate; on setting fire to the vapour at the mouth of the tube it burns with a green flame.

The original sodium compound, $C_{34}H_{27}NaO_6 \cdot C_2H_5O$, does not readily give good figures for sodium and alcohol, owing to the fact that it is very difficult to expel the whole of the alcohol of crystallisation without decomposing the remaining compound. Loss on heating at 110°: 8.21 to 9.03 per cent.; calculated for 1 mol. C_2H_5O : 7.67 per cent. Na in resulting substance: found 3.99 to 4.55 per cent.; calculated 4.15 per cent.

This sodium compound is, as already mentioned, very soluble in benzene. If a strong benzene solution is allowed to stand for two or three weeks in a corked flask, large, transparent crystals, containing benzene of crystallisation are slowly deposited. These are sparingly soluble in benzene; but on exposure to air, or when gently heated, they effloresce, and the effloresced substance again dissolves readily in benzene.

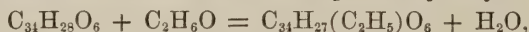
Although ethylic anhydrodibenzilacetate, as some of its other reactions show, undoubtedly contains the carbethoxyl group, it was not found possible to hydrolyse it by means of alkali to the corresponding acid, owing to the ease with which it is decomposed with regeneration of benzil.

No acetyl derivative was obtained by boiling ethylic anhydrodibenzilacetoacetate with acetic anhydride for one hour.

The substance was also heated alone at 150—160° in a flask, previously exhausted by a Sprengel mercury pump. Carbon dioxide was given off, mixed, towards the end of the operation, with a gas which was not absorbed by caustic potash. After the evolution of gas had ceased, the residue in the flask was dissolved in benzene. The solution deposited benzil. No other compound could be isolated from this residue.

Phenylhydrazine does not act on the compound in boiling alcoholic solution. At a higher temperature the dihydrazone of benzil is obtained.

Action of Ethylic Alcohol and Sulphuric acid on Ethylic Anhydrodibenzilacetoacetate.—Ten grams of ethylic anhydrodibenzilacetoacetate were boiled for five hours with a mixture of 200 c.c. of absolute alcohol and 10 drops of concentrated sulphuric acid, using a reflux condenser. The substance was precipitated by the addition of water, and purified by recrystallisation from boiling alcohol. It formed slender prisms or needles melting at 197°. (Yield: 5.5 grams of pure substance.) In purifying various preparations of this substance, it was frequently noticed that the mother liquors from the needles melting at 197° deposited, on standing, other needles, very similar to these in appearance, but melting at 178°. On recrystallising the latter substance from alcohol, the melting point at once rose to 197°. The compound thus appears to be dimorphous. Analysis of the substance dried at 100° showed that a hydrogen atom of ethylic anhydrodibenzilacetoacetate had been replaced by ethyl



yielding *ethylic ethylanhydrodibenzilacetoacetate*.

0.1700 gave 0.4791 CO₂ and 0.0893 H₂O. C = 76.86; H = 5.84.

0.2033 „ 0.5742 CO₂ „ 0.1056 H₂O. C = 77.02; H = 5.77.

C₃₆H₃₂O₆ requires C = 77.14; H = 5.71 per cent.

An attempt was made to prepare this compound by heating ethylic anhydrodibenzilsodacetoacetate in benzene solution in a sealed tube with ethylic iodide. A separation of sodium iodide occurred, showing that an interaction had taken place; but the benzene solution, on evaporation, yielded a large quantity of benzil. A very minute quantity of a substance crystallising in tufts of needles was also formed, quite insufficient for further investigation.

It is, therefore, probable that sodium and ethyl replace different hydrogen atoms of the condensation compound.

Of the two ethyl groups contained in the molecule of ethylic ethylanhydrodibenzilacetoacetate, that which was already present in

the condensation compound is in the ester form; that which was afterwards introduced by the etherification with alcohol and sulphuric acid is in the ether form. Only the former ethyl group is removed by hydrolysis with caustic alkali.

Ethylanhydrodibenzilacetoacetic acid.—Ethylic ethylanhydrodibenzilacetoacetate was heated with alcoholic potash for half an hour on the water bath. On standing over night, the solution deposited prismatic crystals of a potassium salt. (In a subsequent preparation it was found that the addition of more alcohol facilitated the crystallisation of this salt.) The crystals were separated by filtration through a platinum cone, and washed with alcohol. They were practically insoluble both in alcohol and in water, but dissolved on warming with water containing a little alcohol. The organic acid was precipitated by dilute sulphuric acid, and purified by recrystallisation from hot benzene. The benzene solution deposited the substance in a form which appeared to the eye amorphous, but under the microscope was seen to consist of minute matted needles. It melted constantly at 216° . 5.5 grams of ester yielded 3.5 grams of acid. Analysis of the substance dried at 100° gave figures agreeing with the expected formula of *ethylanhydrodibenzilacetoacetic acid*, $C_{32}H_{23}(C_2H_5)O_6$.

0.2348 gave 0.6603 CO_2 and 0.1130 H_2O . C = 76.69; H = 5.34.

0.1453 „ 0.4083 CO_2 „ 0.0708 H_2O . C = 76.63; H = 5.41.

$C_{34}H_{28}O_6$ requires C = 76.69; H = 5.26 per cent.

It is isomeric with the condensation compound.

The *silver salt* was obtained by precipitating a solution of the ammonium salt in dilute alcohol with an aqueous solution of silver nitrate. It formed a white precipitate, which showed a tendency to become dark coloured. It was dried in a vacuum desiccator.

0.2918 gave, on ignition, 0.0500 Ag. Ag = 17.13.

$C_{34}H_{27}O_6Ag$ requires Ag = 16.90 per cent.

The *barium salt* was obtained in a similar manner, precipitating with barium chloride. It was recrystallised from a mixture of water with rather more than its volume of alcohol, and was thus obtained in small prisms. For analysis it was dried at 100° .

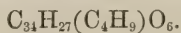
0.3614 gave 0.0694 $BaSO_4$. Ba = 11.29.

$(C_{34}H_{27}O_6)_2Ba$ requires Ba = 11.43 per cent.

In order to prove that the ethyl group, which is removed during the hydrolysis of ethylic ethylanhydrodibenzilacetoacetate to the acid is, as already stated, that which was already present in the condensation compound, we next prepared ethylic isobutylanhydrodibenzilacetoacetate, and subjected it to hydrolysis. Only the ethyl group

was removed, and isobutylanhydrodibenzilacetoacetic acid was formed.

Action of Isobutylic Alcohol and Sulphuric acid on Ethylic Anhydrodibenzilacetoacetate.—Ten grams of ethylic anhydrodibenzilacetoacetate were boiled with a mixture of 200 grams of isobutylic alcohol and 50 drops of concentrated sulphuric acid for five hours. About half the liquid was then distilled off, and the remainder poured into water, which occasioned the separation of a viscid mass. By repeated recrystallisation from a mixture of benzene and light petroleum the substance was obtained in minute needles melting constantly at 192° . Analysis of the compound, dried at 100° , gave figures agreeing with those required for *ethylic isobutylanhydrodibenzilacetoacetate*,



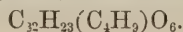
0.1898 gave 0.5395 CO_2 and 0.1093 H_2O . C = 77.52; H = 6.39.

0.1842 „ 0.5235 CO_2 „ 0.1044 H_2O . C = 77.51; H = 6.29.

$\text{C}_{38}\text{H}_{26}\text{O}_6$ requires C = 77.55; H = 6.12 per cent.

In a subsequent preparation of this compound we obtained a small quantity of a substance identical in appearance with the foregoing, but melting constantly at 202° . As it gave practically the same figures on analysis (Found: C = 77.57; H = 6.69 per cent.), the hydrogen alone being somewhat higher, we assumed that it was the same compound, but in a purer condition, and in a preliminary note (Proc., 1895, 147) we gave 202° as the melting point of the compound. It is possible, however, that this second substance may be *isobutylic isobutylanhydrodibenzilacetoacetate*, $\text{C}_{40}\text{H}_{40}\text{O}_6$ (Calculated: C = 77.92; H = 6.49 per cent.), formed from the ethylic ester by the displacement of ethyl by isobutyl under the influence of the sulphuric acid. We must, therefore, leave the question of the correct melting point open.

Isobutylanhydrodibenzilacetoacetic acid.—The hydrolysis of ethylic isobutylanhydrodibenzilacetoacetate (m. p. 192°) was carried out exactly as in the case of the ester already described, except that, as the potassium salt did not separate so readily in the present case, the solution in alcoholic potash was diluted with water, warmed until any salt redissolved, and precipitated with dilute sulphuric acid. The new acid was somewhat difficult to purify. From its solution in benzene it was deposited in dark-coloured crystals. The best result was obtained by dissolving the acid in boiling ethylic acetate and diluting with light petroleum. The substance was deposited in colourless slender needles melting constantly at 237° . Analysis of the compound, dried in a vacuum desiccator, gave figures agreeing with the formula of *isobutylanhydrodibenzilacetoacetic acid*,



0.1634 gave 0.4613 CO_2 and 0.0863 H_2O . $\text{C} = 76.99$; $\text{H} = 5.84$.
 0.1741 „ 0.4928 CO_2 „ 0.0907 H_2O . $\text{C} = 77.19$; $\text{H} = 5.78$.

$\text{C}_{36}\text{H}_{32}\text{O}_6$ requires $\text{C} = 77.14$; $\text{H} = 5.71$ per cent.

The *silver salt* and the *barium salt* were prepared like the corresponding salts of the ethyl acid.

The silver salt was obtained as a white precipitate. It was dried in a vacuum desiccator.

0.2908 gave, on ignition, 0.0462 Ag. $\text{Ag} = 15.88$.

$\text{C}_{36}\text{H}_{31}\text{O}_6\text{Ag}$ requires $\text{Ag} = 16.19$ per cent.

The barium salt was recrystallised from dilute alcohol, from which it was deposited in slender needles. It was dried at 100° .

0.4362 gave 0.0792 BaSO_4 . $\text{Ba} = 10.68$.

$(\text{C}_{35}\text{H}_{31}\text{O}_6)_2\text{Ba}$ requires $\text{Ba} = 10.92$ per cent.

Oxidation of Ethylic Anhydrodibenzilacetoacetate.—Ten grams of the condensation compound were dissolved in glacial acetic acid, and to the warm solution 10 grams of chromium trioxide, also dissolved in glacial acetic acid, were gradually added. Considerable heat was evolved, and the reaction was completed without further warming. Addition of water precipitated an organic substance, which was separated by filtration and treated with a solution of sodium carbonate to remove acids; the residue was apparently chiefly unchanged substance. The acids were reprecipitated with sulphuric acid and treated with a little ether to remove benzoic acid; the organic acid which remained was dissolved in ethylic acetate, and light petroleum added; the solution deposited slender needles melting constantly at 200° with evolution of gas. The yield of acid in different preparations was not more than from 1 to 1.5 gram from 10 grams of the condensation compound. Analysis gave figures which led to the formula $\text{C}_{22}\text{H}_{16}\text{O}_4$.

0.1492 gave 0.4208 CO_2 and 0.0640 H_2O . $\text{C} = 76.92$; $\text{H} = 4.76$.

0.1932 „ 0.5456 CO_2 „ 0.0794 H_2O . $\text{C} = 77.02$; $\text{H} = 4.56$.

$\text{C}_{22}\text{H}_{16}\text{O}_4$ requires $\text{C} = 76.74$; $\text{H} = 4.65$ per cent.

The *silver salt* was prepared by precipitating an aqueous solution of the ammonium salt with silver nitrate. It formed a white powder which did not darken appreciably at 100° .

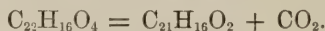
0.4437 gave, on ignition, 0.1028 Ag. $\text{Ag} = 23.70$.

$\text{C}_{22}\text{H}_{15}\text{O}_4\text{Ag}$ requires $\text{Ag} = 23.95$ per cent.

We give reasons later on for regarding this acid as *phenyldibenzoylacetic acid*.

Action of Heat on Phenyldibenzoylacetic acid.—In order to ascertain the nature of the decomposition occurring at the melting point of

this acid, 5 grams of the substance were introduced into an Anschütz distilling flask (with receiver fused on), the flask was exhausted by means of a Sprengel mercury pump, and then heated to 200° . At this temperature a gas was evolved, which was found to be pure carbon dioxide; the fused acid assumed a deep violet colour. As soon as the evolution of gas had ceased the residue was distilled under reduced pressure; it passed over at $300\text{--}305^{\circ}$ under a pressure of about 15 mm. The distillate, which formed a clear brown resin, was dissolved in hot alcohol; from a dilute solution it was deposited in flat needles melting constantly at $119\text{--}120^{\circ}$. The yield in the foregoing experiment was only 1.5 gram. The substance is insoluble in aqueous caustic alkalis. Analysis gave figures agreeing best with the formula $\text{C}_{21}\text{H}_{16}\text{O}_2$, the compound having been formed from the acid according to the equation

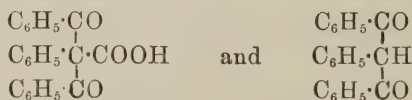


0.1250 gave 0.3856 CO_2 and 0.0574 H_2O . C = 84.13; H = 5.10.

0.1024 „ 0.3162 CO_2 „ 0.0492 H_2O . C = 84.20; H = 5.33.

$\text{C}_{21}\text{H}_{16}\text{O}_2$ requires C = 84.00; H = 5.33 per cent.

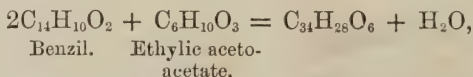
The following formulæ might express the constitution of the acid and its product of decomposition.



Phenyldibenzoylacetic acid. Phenyldibenzoylmethane.

The following considerations appear to favour the foregoing formula for the acid.

The condensation compound, $\text{C}_{34}\text{H}_{28}\text{O}_6$, being formed according to the equation



must contain in its molecule four $\text{C}_6\text{H}_5\cdot\text{C}$ groups derived from benzil. In the oxidation of the compound each $\text{C}_6\text{H}_5\cdot\text{C}$ group, if removed, must be removed as a whole. In the formation of an acid of the formula $\text{C}_{22}\text{H}_{16}\text{O}_4$, one $\text{C}_6\text{H}_5\cdot\text{C}$ group has been so removed. The three which remain account for $\text{C}_{21}\text{H}_{15}$, that is, for all the carbon and hydrogen in the molecule of the acid except the one atom of each of these elements required for the carboxyl group. This carbon atom of the carboxyl group is all that remains of the molecule of ethylic acetoacetate. The foregoing mode of formulating the acid as phenyldibenzoylacetic acid seems, therefore, to be the most natural. Indeed, the only alternative constitution, so far as we can see, would be

$C_6H_5 \cdot CO \cdot O \cdot C(C_6H_5) : C(C_6H_5) \cdot COOH$, which is the formula of a benzoate derived from the enolic form of deoxybenzoïncarboxylic acid. Such a compound would, however, be readily hydrolysed to benzoic acid and deoxybenzoïncarboxylic acid, the latter thereafter breaking up into deoxybenzoïn and carbon dioxide; but the present acid, when heated with a solution of caustic alkali, is stable. Moreover, it would be necessary to assume the existence of this complex in the molecule of the condensation compound—an assumption quite out of keeping with the ease with which the latter compound regenerates benzil.

It might be objected that the acid is too stable to have the constitution of a β -ketonic acid. W. H. Perkin, jun., has, however, shown that, although benzoylacetic acid, when heated to its melting point (104°), parts with carbon dioxide, dibenzoylacetic acid, on the other hand, melts at 109° without decomposition, and may even, in small quantities, be distilled undecomposed. The introduction of a phenyl group into the molecule of dibenzoylacetic acid would in all probability give it the stability of the acid under consideration.

From the formula of the acid, that of the diketone follows as a matter of course.

The chief objection to this mode of formulating these compounds lies in the fact that the supposed diketone does not interact with phenylhydrazine even at the boiling point of the latter, whereas it might have been expected to yield with it tetraphenylpyrazole, just as Knorr (*Annalen*, 1894, **279**, 235) has prepared tetramethylpyrazole by the interaction of methylhydrazine with methylacetylacetone (methyldiacetylmethane). It may be, however, that there are stereochemical reasons for the non-existence of a tetraphenylpyrazole, just as there is a tetramethylmethane, but no tetraphenylmethane.

The insolubility of the diketone in aqueous caustic alkalis would indicate that it has no tendency to assume the enolic form which is necessary to the formation of a pyrazole. But of course it might interact with phenylhydrazine without forming a pyrazole.

Attempts which we made to introduce a benzoyl group into the molecule of deoxybenzoïn, so as to synthesise a compound of the formula of the foregoing diketone, proved unsuccessful.

If the foregoing formulæ are correct, it follows that, in the formation of the condensation compound, the two benzil complexes become united to one another by carbon bonds, and, further, that the acetoacetic group enters into similar union with the resulting dibenzil complex.

Reduction of Ethylic Anhydrodibenzilacetoacetate and its Ethyl and Isobutyl Derivatives with Hydriodic acid.—Finely powdered ethylic anhydrodibenzilacetoacetate was boiled for about three minutes with

excess of fuming hydriodic acid, shaking the flask during the whole operation. The substance fused. Water was then added, the liquid extracted with ether, and the ethereal extract was shaken with a dilute solution of sulphur dioxide to remove iodine, then with water, and finally with a solution of sodium carbonate. The latter solution was found not to have taken up any organic acid. During the process a portion of the reduction product separated from the ether in a crystalline form. The ether, on evaporation, left a gummy mass; this was dissolved in ethylic acetate, and light petroleum added; the liquid deposited lustrous, short prisms, which, after recrystallisation, melted without decomposition constantly at 187—188°. Analysis of substance dried at 50° gave the following figures.

0.1736 gave 0.5732 CO₂ and 0.0903 H₂O. C = 90.05; H = 5.77.

0.1545 „ 0.5096 CO₂ „ 0.0823 H₂O. C = 89.94; H = 5.91.

C₂₈H₂₂O requires C = 89.84; H = 5.88 per cent.

In our previous note on this subject (Proc., 1895, 147) we deduced from these results the formula C₃₁H₂₄O (calculated, C = 90.29; H = 5.83 per cent.), assuming that, along with the reduction, there had been an elimination of the carbethoxyl group from the condensation compound. Since then, however, we have reduced the ethyl and isobutyl derivatives of the condensation compound, both of which also yield the foregoing substance melting at 187—188°; but along with this we obtained from the ethyl derivative, by boiling for a short time with the hydriodic acid, a compound C₂₈H₂₂O₂ (m. p. 221°) as an intermediate product. The higher proportion of oxygen in this compound enables its formula to be calculated with greater certainty, and as it is converted by longer boiling with the hydriodic acid into the compound of m. p. 187—188°, we must assume that the latter is its reduction product and has the formula C₂₈H₂₂O.

The foregoing illustrates the difficulty of dealing with some of these compounds. In the case of the compound containing only one atom of oxygen, analysis alone is incompetent to decide the formula. We did not attempt a Raoult determination, as the method is not sufficiently accurate for the present purpose.

Neither acetic anhydride at its boiling point, nor phenylhydrazine in alcoholic solution at 150°, had any action on the compound C₂₈H₂₂O₂.

The reduction in the case of the ethyl and isobutyl derivatives was carried out as described in the case of ethylic anhydrodibenzilacetate, and the mode of purification of the product was also the same. In the case of the ethyl derivative we found, as just stated, that by boiling for a short time (under five minutes) with the hydriodic acid, a compound was obtained crystallising in needles melting

at 221° ; whereas if the substance was boiled for longer (seven minutes) the compound $C_{25}H_{22}O$, crystallising in short prisms melting at 187 — 188° was formed. The compound melting at 221° was purified by crystallisation, first from ethylic acetate, afterwards from glacial acetic acid. Analysis gave figures agreeing with the formula $C_{28}H_{22}O_2$.

0.1215 gave 0.3335 CO_2 and 0.0643 H_2O . C = 86.08; H = 5.79.

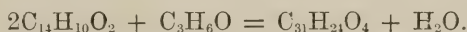
0.1388 „ 0.4384 CO_2 „ 0.0707 H_2O . C = 86.14; H = 5.66.

$C_{28}H_{22}O_2$ requires C = 86.15; H = 5.64 per cent.

The isobutyl derivative gave as chief product of reduction the compound $C_{25}H_{22}O$ (m. p. 187 — 181°); but along with it another crystalline substance melting at 155° . The quantity was too small for further investigation; but the substance appeared to be identical with a compound melting at 155 — 159° obtained in the reduction of anhydracetonedibenzil (see following section).

If the formulæ containing 28 atoms of carbon correctly express the composition of the reduction compounds, it is evident that the hydriodic acid completely removes the acetoacetic group from the condensation compound and its derivatives, only the dibenzil complex remaining.

Reduction of Anhydracetonedibenzil with Hydriodic acid.—The mode of formation of ethylic anhydrodibenzilacetoacetate is strictly analogous to that of anhydracetonedibenzil, which, as Japp and Miller have shown (Trans., 1885, 47, 34), is formed from benzil and acetone according to the equation



It thus appeared probable that ethylic anhydrodibenzilacetoacetate was the carbethoxyl derivative of anhydracetonedibenzil. We therefore reduced the latter compound with hydriodic acid, in order to ascertain whether it would yield the same products as the former.

The reduction was carried out as already described. A product was obtained which was deposited from a mixture of ethylic acetate and light petroleum in two forms; small, lustrous prisms melting at 187 — 188° , identical with the reduction product of ethylic anhydrodibenzilacetoacetate; and larger crystals, of pyramidal habit, melting at 155 — 159° . The two forms were separated mechanically and then further purified by recrystallisation. The melting points were unchanged. Both substances gave figures agreeing with the formula $C_{25}H_{22}O$.

Small prisms (m. p. 187 — 188°).

0.2281 gave 0.7490 CO_2 and 0.1193 H_2O . C = 89.55; H = 5.81.

$C_{25}H_{22}O$ requires C = 89.84; H = 5.88 per cent.

Pyramids (m. p. 155—159°).

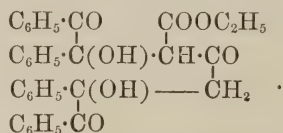
0.1428 gave 0.4706 CO₂ and 0.0758 H₂O. C = 89.88; H = 5.89.

C₂₈H₂₂O requires C = 89.84; H = 5.88 per cent.

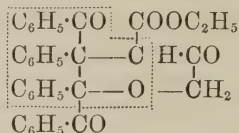
We also oxidised anhydracetonedibenzil with chromium trioxide in acetic acid solution, in order to ascertain whether phenyldibenzoylacetic acid was formed, but did not succeed in identifying this substance among the products of oxidation.

Constitution of Ethylic Anhydrodibenzilacetoacetate.—It is perhaps premature, on the strength of the foregoing very imperfect study of this substance, to attempt to assign to it a constitutional formula; and the following must therefore be regarded as merely a provisional expression which, as far as it goes, appears to us to account for the reactions here described.

That two molecules of benzil interact with one of ethylic acetoacetate must be ascribed to the fact that the latter compound contains two groups—methylene and methyl—both of which, owing to their mode of combination, are capable of undergoing condensation with the carbonyl groups of benzil. If we assume that the first stage of the interaction is the double occurrence of an aldol condensation, we should have, as an intermediate product,



This hypothetical intermediate compound must then part with a molecule of water, and at the same time the two benzil residues must become united by means of carbon bonds, so as to account for the formation of phenyldibenzoylacetic acid on oxidation. To satisfy these conditions, we must assume the occurrence of some such rearrangement as the following:

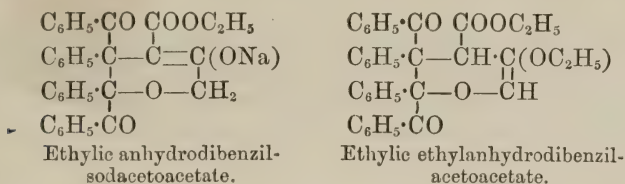


Ethylic anhydrodibenzilacetoacetate.

The portion of the formula enclosed by the dotted line represents that part of the molecule which, in the process of oxidation, forms phenyldibenzoylacetic acid. In this process, the lower benzoyl group in the formula is removed in preference to the upper, because it is attached to a carbon atom which is already partially oxidised.

The sodium derivative on the one hand, and the alkyl derivatives

on the other, in which, as has been shown, metal and alkyl replace different hydrogen atoms of the condensation compound, are to be regarded as derived from two distinct enolic forms of the foregoing.



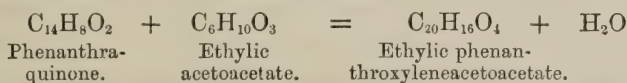
The sodium compound being formulated on the analogy of ethylic sodacetoacetate; the ethyl derivative on a different type. These formulæ would explain why the ethyl derivative cannot be obtained by the action of ethylic iodide on the sodium compound; also why the alkylated acids are stable, and anhydrodibenzilacetoacetic acid itself so unstable that it could not be obtained from its ester; the reason being that the latter acid is a β -ketonic acid, whilst the alkylated acids are substituted unsaturated acids.

An objection might be raised to the foregoing formula for ethylic anhydrodibenzilacetoacetate on the ground that in a compound of this constitution, the acetoacetic group should not be removable by hydriodic acid. A precisely similar separation of carbon from carbon in the course of a hydriodic acid reduction has, however, been observed by Japp and Wadsworth (Trans., 1890, 57, 971) in the case

of paradesylphenol, $\text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, where a separation of the desyl group from the nucleus of the phenol occurs. Moreover, as the carbon atom of the carboxyl group of the phenyldibenzoylacetic acid obtained from ethylic anhydrodibenzilacetoacetate by oxidation, is furnished, as we have already shown, by the ethylic acetoacetate, the existence of this carbon linkage must be granted.

The constitutional formula of anhydracetonedibenzil, $\text{C}_{31}\text{H}_{24}\text{O}_4$, may be derived from that of ethylic anhydrodibenzilacetoacetate by substituting hydrogen for the carbethoxyl group.

In conclusion we may call attention to the totally different character of the interaction of ethylic acetoacetate with benzil and phenanthraquinone respectively. In the latter case, one molecule of each substance takes part in the condensation.



(Japp and Streatfeild, Trans., 1883, 43, 27; Japp and Klingemann, Trans., 1891, 59, 1). In fact, there are hardly any reactions in the

whole range of organic chemistry more erratic than the condensations of the α -diketones with ketones and ketonic acids; it is hardly possible to say beforehand what course the reaction will take in any particular case.

The study of the condensation of benzil with ethylic acetoacetate was begun in 1888 by one of us in conjunction with Dr. Felix Klingemann, who prepared the condensation compound and its ethyl derivative; but, owing to pressure of other work, it was at that time postponed.

*Chemical Department,
University of Aberdeen.*

XLIV.—*Electrolysis of Potassium Allo-ethylic Camphorate. Part II.*

By JAMES WALKER, Ph.D., D.Sc., and JAMES HENDERSON, B.Sc.,
University College, Dundee.

IN our former communication (Trans., 1895, **67**, 337), we showed that the chief products of the electrolysis of a concentrated aqueous solution of potassium allo-ethylic camphorate are the ethylic salts of a monobasic acid, $C_9H_{14}O_2$, and of a dibasic acid, $C_{18}H_{30}O_4$, to which we gave the names of allo-campholytic and allo-camphothetic acids respectively. Besides these ethereal salts, the presence of others was indicated, and an attempt has now been made to isolate some of them.

A quantity of potassium allo-ethylic camphorate was prepared, and electrolysed in the manner described in our previous paper, the ethereal product obtained being then subjected to repeated fractional distillation, first under diminished pressure, and, finally, at the pressure of the atmosphere. In order to ascertain the probable positions of the different ethereal liquids in the fractions boiling below 265° at 760 mm., the sp. gr. and the rotatory power of each fraction of 5° were determined. The density at $16^\circ/4^\circ$ increased continuously from 0.949 for fraction 200— 205° , to 1.043 for fraction 260— 265° . The rotatory power, on the other hand, exhibited much greater variation, falling from $[\alpha]_D = +29.8$ for 200— 205° to a minimum of 14.7 for 230— 235° , thereafter increasing rapidly to 41.4 at 255— 260° , again to diminish in the fractions with higher boiling points.

By far the largest fractions were obtained in the neighbourhood of 200° , the chief product being, as before, the ethylic salt of allo-

campholytic acid, which boils at 204° . The rotatory power on this occasion, however, fell far short of the specific rotation of the ethylic allo-campholytate formerly prepared. We found (*loc. cit.*, 340) for this substance $[\alpha]_D = +39.1$, whilst for the fraction $200-205^{\circ}$ we have now only $[\alpha]_D = +29.8$. We were at first inclined to attribute this difference to a diminution of the rotatory power caused by the repeated distillation, but on redistilling the ethereal salt several times the rotations remained practically constant. It was, therefore, probable that in this fraction of nearly constant boiling point there were at least two isomeric substances whose boiling points were close together, but whose rotatory powers lay widely apart, one of them being ethylic allo-campholytate with the rotation of at least $+39$, the other an isomeride with a much smaller positive, or even a negative rotation.

It is not surprising that the ethereal salt with negative or small positive rotatory power should be present in the product of the second electrolysis in greater proportion than was the case in the first experiment; for it has been repeatedly shown that very slight variations in the conditions of electrolysis may cause considerable variations in the relative quantities of the products obtained. The specific rotation $[\alpha]_D = +39.1$ given for ethylic allo-campholytate is doubtless somewhat too low, for the isomeric substance was not altogether absent, even in the first electrolysis, although, as will presently appear, the amount of this impurity must have been small; the actual number, therefore, can only be slightly higher than that given.

During the distillation of the acid obtained by saponifying the ethylic campholytate with alcoholic potash and acidifying, we had previously been struck by the appearance in the condensed liquid of a dark green coloration, which vanished on heating. No explanation of this was found at the time, but the repetition of the experiment with the second supply of material served to account for the phenomena observed. The fractions boiling below 210° , 54 grams in all, were heated for two hours on the water bath with 30 grams of caustic potash dissolved in alcohol; the alcohol was distilled off, and steam passed through the residue in order to remove any unaltered ethereal salt. Excess of hydrochloric acid was then added to liberate the allo-campholytic acid, and this was extracted from the aqueous liquid with ether, dried, and fractionated at the ordinary pressure.

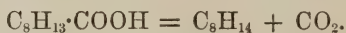
On distillation, practically nothing passed over until the temperature approached 200° , when lively ebullition set in, the thermometer fluctuating unsteadily between 170° and 200° , according to the size of the flame employed. As the amount of liquid distilling over seemed much greater than corresponded to the heat supply, the

flame was removed, and it was observed that the ebullition went on for a considerable time spontaneously, the temperature registered by the thermometer remaining fairly constant at 170° . The liquid in the distilling flask did not blacken, and the distillate was of the green colour previously noticed. These results could only be explained by the assumption that decomposition had taken place, a supposition which was confirmed by the fact that the uncondensed gas passing into the receiver was almost pure carbonic anhydride.

After a time, the decomposition ceased and the temperature rose rapidly to 230° , by far the greater part of the liquid distilling over at 232 — 235° . This portion consisted of allo-campholytic acid (b. p. 233 — 235°). The lower boiling portions were then refractionated, and it was plainly evident that decomposition had occurred, for now the liquid passed over almost completely between 120° and 124° , the slight residue left being of much higher boiling point. On redistillation, the liquid boiled at 120 — 122° .

Hydrocarbon, C_8H_{14} .

The distillate thus obtained was a light neutral oil of pleasant, aromatic odour, and of a feeble yellow colour. On exposure to air its colour deepened to brown, and occasionally, on distillation, a fine green was developed in the condensed liquid. From its boiling point and neutral character, the substance appeared to be a hydrocarbon, probably unsaturated on account of its alterability on exposure to air. As the other product of the decomposition was carbonic anhydride, and as no blackening or other sign of complete destruction of the molecule occurred, the action was probably the splitting up of an isomeride of allo-campholytic acid by heat, according to the equation



Elementary analysis supported this conclusion.

0.0543 gave 0.1726 CO_2 and 0.0628 H_2O . C = 86.7; H = 12.8.

C_8H_{14} requires C = 87.3; H = 12.7.

The unsaturated nature of the hydrocarbon was rendered evident by its action on alkaline permanganate and on bromine, both of which it at once decolorised.

The ethereal product of electrolysis, boiling at 200 — 210° , thus contains the ethylic salts of two acids, one of which, allo-campholytic acid, may be distilled unchanged; whereas the other isomeric acid breaks up at about 200° into the hydrocarbon, C_8H_{14} , and carbonic anhydride. Very little of the latter acid was present in the product of our first electrolysis, for the hydrocarbon derived from it existed in such small quantity that it was not detected in the distillation,

although it imparted its colour (or rather that of its oxidation products) to the distillate.

References to hydrocarbons of the formula C_8H_{14} are frequent in the literature of camphoric acid and its derivatives. The following table gives the origin, boiling point, and density of the hydrocarbons obtained by various investigators.

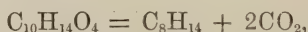
Reference.	Source.	B. p.	Sp. gr.
1. Wreden, <i>Annalen</i> , 1877, 187 , 171	Camphanic acid } Camphoric acid }	119°	0·793 at 19°/4°
2. Reyher, Inaug.-Diss., Leipzig, 1891, 51	Camphanic acid ..	122	—
3. Aschan, <i>Annalen</i> , 1896, 290 , 185	„ ..	119	0·802 at 18°/4°
4. Noyes, <i>Ann. Chem. Jour.</i> , 1895, 17, 432	Aminolauronic acid	122	0·802 at 15°/4°
5. Kœnigs and Meyer, <i>Ber.</i> , 1894, 27 , 3470	Sulphocamphylic acid Isocampholytic acid	108—110	0·795 at 15°
6. Damsky, <i>Ber.</i> , 1887, 20 , 2959	Sulphocamphylic acid	108—110	0·795 at 11°/11°
7. Moitessier, <i>Jahresber.</i> , 1866.	Copper camphor- ate	105	0·793
8. Wreden, <i>loc. cit.</i>	Camphoric acid...	104—107	0·800 at 0°

It would appear from these results that there are (apart from stereoisomeric considerations) two hydrocarbons, C_8H_{14} , derivable from camphoric acid, one boiling at about 120°, the other at about 108°. Both may be obtained from camphoric acid or its salts directly, but when the source is an acid derived from camphoric acid, then only one of the hydrocarbons is generated. Thus camphanic acid and aminolauronic acid yield the hydrocarbon boiling at 120°, whilst sulphocamphylic acid and isocampholytic* acid yield the other isomeride. This corresponds to the genetic relations of the different substances. There are genetically connected with each other two series of camphoric acid derivatives. To one series belong campholytic acid, sulphocamphylic acid, iso-campholytic acid; to the other allo-campholytic acid, aminolauronic acid, lauronic acid, camphanic acid, and the campholactones. The hydrocarbon boiling at 108° is derivable from the compounds of the first series; the hydrocarbon boiling at 120° from the compounds of the second.

* The nomenclature of the isomeric acids, $C_8H_{13} \cdot COOH$, is at present somewhat confused. Four isomerides are known: (1) campholytic acid = *cis-trans*-campholytic acid (Noyes); (2) isocampholytic acid = *cis*-campholytic acid (Noyes) = isolauronic acid (Kœnigs); (3) allocampholytic acid = γ -lauronic acid (Noyes); (4) lauronic acid.

Now, the difference between the two series is that the compounds of the first retain one of the two carboxyl groups of camphoric acid, whilst the compounds of the second retain the other carboxyl group of the original substance. It is true that camphanic acid retains both, but on heating it loses one with formation of lauronolic acid, so that it may be ranked along with that compound. By the electrolysis of sodium ortho-ethyl camphorate, campholytic and iso-campholytic acids are produced; by the electrolysis of sodium allo-ethyl camphorate, we obtain allo-campholytic acid and the isomeric acid which decomposes with formation of C_8H_{14} . As the latter acid must also have its carboxyl group in the allo-position, the hydrocarbon derived from it should correspond to the second series of hydrocarbon derivatives, that is, be identical with that obtained from camphanic acid. This conclusion is borne out in the first place by the boiling-point of our hydrocarbon which is $120-122^\circ$, no indication of a substance of lower boiling point being observed.

The hydrocarbon obtained from camphanic acid according to the equation



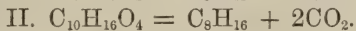
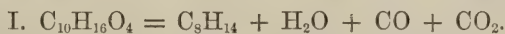
has been recently thoroughly investigated by Aschan (*loc. cit.*), who has given to it the name *laurolene*. The quantity of substance at our disposal was unfortunately too small to enable us to effect an accurate numerical comparison of its physical properties with those of laurolene, but the general resemblance leaves little doubt as to their identity. The density of our hydrocarbon at $16^\circ/4^\circ$ was found to be 0.798; that of laurolene at $18^\circ/4^\circ$ is given by Aschan as 0.802. The hydrocarbon obtained by us was optically active, rotating the plane of polarisation to the left. Aschan gives $[\alpha]_D = -23.0$ as the specific rotatory power of laurolene. We had not sufficient material to determine the rotatory power of our substance in the pure state, but we found that in 25 per cent. ethereal solution (by volume), its specific rotatory power was $[\alpha]_D = -29.2$.

The chemical properties of the two substances are exactly alike. Besides those already mentioned, depending on the unsaturated nature of the compound, we may refer to the behaviour of the hydrocarbon towards nitric acid. Wreden, who originally prepared the substance of boiling-point 120° , states that, when gently warmed with a mixture of nitric and sulphuric acids, it is partially converted into trinitrometaxylene. Aschan on the other hand found that laurolene was violently acted on by strong nitric acid alone, and also by a mixture of nitric and sulphuric acids, but by cooling with ice, he succeeded in moderating the action, and on subsequent careful warming found that the hydrocarbon disappeared. The whole product, however, was then soluble in water, with the exception of a "scarcely

weighable flocculent precipitate." The behaviour of our hydrocarbon was similar. When added to a nitrating mixture, it was at once attacked with evolution of torrents of red fumes, and if the mixture contained in a flask were even slightly above the laboratory temperature, the addition of a drop of the hydrocarbon was followed by a flash and sharp report. By keeping the mixture in ice and allowing the action to proceed slowly we arrived at the same result as Aschan—on pouring into water nothing separated but a few flocks of a pale yellow substance in quantity too small to be collected.

When this behaviour is compared with that of Wreden's hydrocarbon, apparently prepared by the same method as that employed by Aschan, the contrast is great. There can be no reasonable doubt that Wreden actually obtained trinitrometaxylene from his hydrocarbon, for he gives the analysis of the product, and the yield (10 per cent. of the hydrocarbon taken); and he nowhere indicates that the nitration presented any difficulty, merely stating that he warmed with a mixture of nitric and sulphuric acids.

These seemingly contradictory results may yet, we think, be reconciled. Wreden first of all prepared the hydrocarbon of boiling-point 120° from camphanic acid (*Annalen*, 1872, **163**, 336) and partially investigated its properties. In his later paper, however (*Annalen*, 1877, **187**, 171), he continued his investigation with a hydrocarbon prepared by the action of hydriodic acid of sp. gr. 1.7 on camphoric acid at 200° . A previous experiment had shown that camphoric acid on heating at 200° with hydrochloric acid saturated at 0° , yields 15 per cent. of a hydrocarbon, which he analysed, and states to be a mixture of C_8H_{14} and C_8H_{16} . These compounds he looked upon as being produced from camphoric acid according to the equations



A consideration of his analytical results indicates that the mixture must have contained a large proportion of C_8H_{16} , possibly as much as half. The yield of hydrocarbon when hydriodic acid was used instead of hydrochloric acid he found to be much more satisfactory—equal to 31 per cent. of the camphoric acid taken, so that he adopted this method of preparing the substance. Although he explicitly notes that the hydrocarbon C_8H_{14} produced in this way contains an admixture of C_8H_{16} , he curiously enough proceeds with the determination of its properties as if it were C_8H_{14} , without any further purification than simple distillation. Now, this process is entirely inadequate to separate the two hydrocarbons, for the boiling point of C_8H_{16} is given by Wreden himself as $117\text{--}120^{\circ}$ (*Annalen*, 1877, **187**, 157), and that of C_8H_{14} from camphanic acid as 119° . With

regard to the quantity of C_8H_{16} probably present in the mixture of hydrocarbons studied by Wreden, the following considerations may be adduced. In the first place the proportion of C_8H_{16} in the hydrocarbons obtained from camphoric acid by treatment with hydrochloric acid is at least 30 per cent., so that when a hydrogenising agent like hydriodic acid is substituted for hydrochloric acid, one would expect the proportion of the more highly hydrogenised product to be still greater. Secondly, Wreden prepared pure C_8H_{16} from camphoric acid with hydriodic acid of the same specific gravity as above by simply prolonging the time of heating at 200° . It is evident, then, that the hydrocarbon which Wreden subjected to nitration consisted to a great extent, probably much more than half, of the saturated cyclic hydrocarbon, C_8H_{16} . Unfortunately he made no analysis of this product, but contented himself with a determination of its vapour density, which of course is worthless as a distinction between two substances so nearly equal in molecular weight as C_8H_{14} and C_8H_{16} . Wreden (*loc. cit.*, p. 159), Aschan (*Ber.*, 1891, **24**, 2722), and Wallach (*Ber.*, 1892, **25**, 922), have proved that the hydrocarbon C_8H_{16} yields trinitrometaxylene on treatment with a nitrating mixture, so that it is practically certain that the trinitrometaxylene obtained by Wreden was not produced from the hydrocarbon C_8H_{14} but from the saturated hydrocarbon, C_8H_{16} , which was undoubtedly mixed with it. The apparent contradiction, then, between the results of Wreden on the one hand, and of Aschan and ourselves on the other, may, we think, in this way be removed.

Attempts to oxidise the hydrocarbon C_8H_{14} led in our hands to the production of only the simple organic acids resulting from almost entire destruction of the molecule. The experience of Aschan with laurolene is similar.

When sodium carbonate acts on the dibromide of campholytic acid, a bromo-hydrocarbon, $C_8H_{13}Br$, is produced (Walker, *Trans.*, 1893, **63**, 502). Since campholytic acid belongs to the first or ortho-series of camphoric acid derivatives mentioned above, the corresponding hydrocarbon C_8H_{14} is that boiling at 108° , so that we should expect the bromohydrocarbon to be a derivative of this substance and not of laurolene, which boils at 120° . A consideration of the boiling points confirms this view; $C_8H_{13}Br$ boils (with some decomposition) at 176° . The difference of boiling point caused by the substitution of a bromine for a hydrogen atom may be seen in the closely analogous case of normal octane, C_8H_{18} , and secondary bromooctane, $C_8H_{17}Br$. The former boils at 125° , the latter at 190° , the difference being 65° . If we subtract this difference from the boiling point of $C_8H_{13}Br$, we obtain 111° , a number pointing to the lower boiling hydrocarbon, C_8H_{14} , as the substance to which the bromo-derivative is related.

Acid, $C_9H_{14}O_3$, *m. p.* 228° .

The fractions of the ethereal product of electrolysis boiling between 240° and 260° , that is, those at and near the second maximum of rotatory power, gave a well characterised acid on saponification with alcoholic potash. After the alcohol had been removed in the ordinary manner, the addition of hydrochloric acid to the aqueous solution of the potassium salt caused the separation of a brownish oil, which was isolated by the usual processes and subjected to distillation; the bulk of the liquid passed over between 260° and 290° , little residue being left. The distillate was dark brown, but perfectly transparent, and no evidence of decomposition was observed. On standing for some time, the oil solidified to a soft, brown, crystalline mass, which was boiled for three quarters of an hour with water and animal charcoal. On filtration, a small quantity of a yellow oil ran through with the aqueous solution, but this was separated by a second filtration, and partially solidified on cooling. From the aqueous solution, colourless crystals were deposited, and, on evaporation, the mother liquor yielded a second crop. These crystals were purified by dissolving them in benzene, and precipitating the solution thus obtained with light petroleum. After a repetition of this process, the melting point no longer changed, the substance then melting sharply at 228° (corr.). The following numbers were obtained on the analysis of different fractions.

0.1026 gave 0.2369 CO_2 and 0.0760 H_2O . C = 63.00; H = 8.23.

0.1808 „ 0.4222 „ 0.1347 „ C = 63.68; H = 8.28.

0.1686 „ 0.3911 „ 0.1275 „ C = 63.26; H = 8.40.

$C_9H_{14}O_3$ requires C = 63.53; H = 8.24 per cent.

The substance had thus the composition $C_9H_{14}O_3$, that is, it contained 1 atom of oxygen more than campholytic acid and its isomerides. Its acid nature was evident from its ready solubility in the weakest alkalis. For neutralisation, 0.0972 gram required 5.68 c.c. of a decinormal solution of baryta, corresponding with 0.584 per cent. of replaceable hydrogen in the acid, the amount required by the formula $C_8H_{13}O \cdot COOH$ being 0.588 per cent.

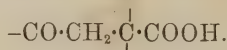
The acid is fairly soluble in cold water (100 parts of the solvent at 17° dissolving 1.4 part acid), and very soluble in boiling water. It is soluble in ether, alcohol, acetic acid, chloroform, acetone, and benzene, very soluble in methylal, and almost insoluble in cold light petroleum. It melts at 228° (corr.), and begins to sublime, without darkening, at 260° —above this temperature, it rapidly becomes brown, boiling freely at about 280° . It does not decolorise bromine in chloroform solution, either in the cold or at the boiling point of the solvent. In sodium carbonate solution, it is not attacked by

potassium permanganate at the ordinary temperature, although, on warming, the colour of the permanganate disappears. These reactions show that the acid contains no ethylene linking. Its solution gave no coloration with ferric chloride, and did not reduce ammoniacal silver nitrate.

A solution of the sodium salt of the acid gave no precipitate with calcium chloride or barium chloride. The silver salt was obtained in the form of a curdy white precipitate, which blackened when the liquid containing it was boiled. Copper sulphate gave a light green precipitate, which dissolved on heating; and lead nitrate a white, crystalline precipitate, also soluble when the mixture was heated. A reddish-brown precipitate was obtained with ferric chloride, which did not dissolve on boiling.

The behaviour of the acid towards bromine and to potassium permanganate is sufficient to show that it is a saturated ring compound. It cannot, therefore, be a hydroxy-campholytic acid, but must rather be a keto-derivative of dihydrocampholytic acid. This supposition receives confirmation from its behaviour on treatment with phenylhydrazine. A solution of phenylhydrazine in excess of aqueous acetic acid was heated at 100° with the acid $C_9H_{14}O_3$; after half an hour, a precipitate began to appear, and, at the expiration of an hour, a sufficient quantity of yellow crystals had separated to permit of their removal and purification. After recrystallisation from glacial acetic acid and from aqueous alcohol, the compound melted at $165\text{--}168^{\circ}$, when heated rapidly. It is soluble in glacial acetic acid, chloroform, benzene, ether, and alcohol, but only very sparingly in light petroleum. It dissolves readily in sodium carbonate solution, and is reprecipitated on the addition of acetic acid.

These results, we think, justify us in concluding that the substance $C_9H_{14}O_3$ is an allo-ketodihydrocampholytic acid, with the ketonic group, most probably, in the γ -position with respect to the carboxyl group. Our reasons for thus locating the $-\text{CO}-$ group are as follows. In the first place, the electrolysis of the metallo-ethereal salts of camphoric acid yields unsaturated acids with the ethylene linking in the $\alpha\beta$ - and $\beta\gamma$ -positions. Unless, therefore, we are to assume that complex intramolecular changes take place, the carbonyl group of the ketonic acid must be in the β - or the γ -position with respect to the carboxyl group. But the properties of our acid are entirely different from those of a β -ketonic acid; and in addition it is derived from the allo-ethylic camphorate, which, as has been pointed out, is genetically connected with such γ -compounds as camphanic acid and campholactone, so that we may assume the acid to contain the grouping



The formation of the ordinary products of electrolysis of salts of saturated carboxylic acids may be most easily explained by the interaction of the negative ions at the anode (compare *Annalen*, **261**, 167; **274**, 41; *Trans.*, **61**, 10; **63**, 495; **67**, 337, 768). At the same time, there is interaction of the anion with water, oxygen being thereby produced, which is either liberated as such or goes to perform work of oxidation. The oxidation at the anode is very frequently complete, the products being carbonic anhydride and water. Occasionally, however, the oxidation is not so far-reaching, and, as von Miller and Hofer have shown (*Ber.*, 1894, **27**, 461), aldehydes and ketones are then not uncommon oxidation products. The formation of the ethylic salt of a monobasic ketonic acid on the electrolysis of the sodium ethylic salt of a dibasic acid is thus not altogether without analogy, and in this case it is of interest on account of the simple relation the compound bears to one of the normal products of reaction between the anions, containing as it does only one more oxygen atom in the molecule than ethylic allo-campholytate.

Constitution of Camphoric acid.

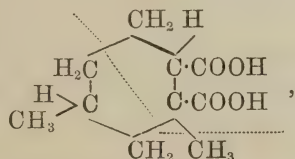
In former papers (*Trans.*, 1893, **63**, 506, and 1895, **67**, 345), it was pointed out that the results of the electrolysis of the metallo-ethereal camphorates were most simply explained on the hypothesis that

camphoric acid contains the complex
$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}\cdot\text{COOH} \\ | \\ -\text{C}\cdot\text{COOH} \end{array}$$
 The nature of

the ketonic acid described above now enables us to assign with some probability the position of another hydrogen atom in the molecule. If it contains the group $-\text{CO}\cdot\text{CH}_2\cdot\text{C}\cdot\text{COOH}$, then camphoric acid must

contain the complex
$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}\cdot\text{COOH} \\ | \\ -\text{C}\cdot\text{COOH} \end{array}$$
 The only published formula

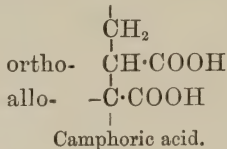
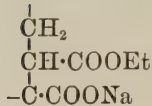
for camphoric acid which agrees with this deduction is that of Armstrong (*Trans.*, 1879, **35**, 757),



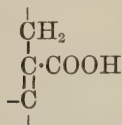
the position of the complex being indicated by the dotted lines.

We may summarise in the following table the information regard-

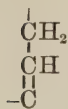
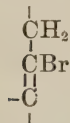
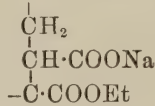
ing the constitution of camphoric acid and its derivatives which is afforded us by the electrolysis of the metallo-ethylic camphorates. Each group in the actual compound is united with a residue C_5H_{11} . The ortho- and allo-carbon atoms have been marked only in the case of camphoric acid itself, their position being supposed to remain unchanged throughout the series.

*Ortho-series.*

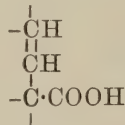
Sodium ortho-ethylic camphorate.



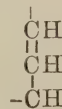
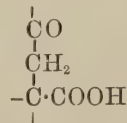
Campholytic acid.

 C_8H_{14} , b. p. 108° . $C_8H_{13}Br$, b. p. 176° .*Allo-series.*

Sodium allo-ethylic camphorate.



Allo-campholytic acid.

 C_8H_{14} , b. p. 120° .Ketonic acid, $C_9H_{14}O_3$.

Noyes has shown that iso-campholytic acid has the same structure as campholytic acid. Lauronic acid probably has the same constitution as allo-campholytic acid, and so too the acid which we found to split up into C_8H_{14} and CO_2 ; the possibility existing that the latter acid may prove identical with lauronic acid, the data concerning which are still somewhat meagre.

The results obtained by Noyes in his investigation of the camphoric acids, and by Aschan in his study of the decompositions of bromo-

camphoric anhydride are in complete accordance with the structural conclusion arrived at in considering the electrolytic decomposition of the camphorates. Any satisfactory camphoric acid formula must therefore account for these mutually confirmatory results. The formulæ recently proposed by Bredt, Tiemann, and Marsh and Gardner take no account of this work, and cannot be brought into harmony with it. When all the evidence is reviewed, it seems that we must at present be content to say with Aschan (*Acta Soc. Scient. Fennica*, 1895, 21, No. 5) that "no formula for camphoric acid hitherto proposed completely accords with all the known facts."

XLV.—*The Explosion of Cyanogen.*

By Professor H. B. DIXON, M.A., F.R.S., E. H. STRANGE, B.Sc., and E. GRAHAM, B.Sc.

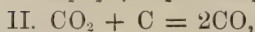
THE experiments described in this paper were undertaken to obtain information on the course of the changes occurring when carbon is oxidised; the oxidation of cyanogen was chosen for investigation as being comparatively simple.

In 1886, one of the authors read a paper before the Chemical Society on the burning of cyanogen (H. B. Dixon, *Trans.*, 1886, **49**, 384). In that paper, it was shown (i) that a spark of considerable intensity was required to initiate an explosion in mixtures of cyanogen and oxygen; (ii) that the presence or absence of moisture made no difference in the readiness with which such mixtures were exploded; and (iii) that the combustion was complete when sufficient oxygen was present to burn the carbon to carbonic acid.

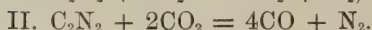
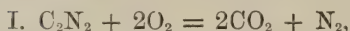
Later experiments (*Phil. Trans.*, 1893, **184**, 97) on the rate of propagation of the "explosion-wave" in gases led to the view that, in the combustion of substances containing carbon, the carbon is first burnt to carbonic oxide, which subsequently is burnt to carbonic acid. In the case of cyanogen, the velocity of the explosion-wave is far higher when the gas is half burnt to carbonic oxide than when there is enough oxygen present to completely burn it. The carbonic oxide found after the explosion of cyanogen with its own volume of oxygen may be formed either by the direct burning of the carbon



or by the burning of half the carbon to carbonic acid, and its subsequent reduction by the rest of the carbon, or by unburnt cyanogen:—



or



Now if half the carbon could burn directly to carbonic acid in the wave front, there seems no good reason why the second half should not burn in the same way if sufficient oxygen were present.* We should expect, therefore, that the velocity of the wave would be greatest when the cyanogen was completely burnt. But this is not the case.

Again, the substitution of inert nitrogen, for the extra oxygen required to complete the burning, produces less retardation than the same volume of oxygen; so far as the propagation of the wave is concerned, the second molecule of oxygen is as inert, weight for weight, as the added nitrogen. The following are the rates observed in metres per second:—

Mixture of gases.	$\text{C}_2\text{N}_2 + \text{O}_2.$	$\text{C}_2\text{N}_2 + 2\text{O}_2.$	$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2.$
Rate of explosion-wave	2728	2321	2398

The same phenomena are shown when cyanogen is exploded with nitrous oxide, and similar facts are presented in the explosion of the hydrocarbons, methane, ethylene, and acetylene. The most natural conclusion to be drawn from these results is that carbonic oxide is the primary product of the explosion of carbon compounds, and the formation of carbonic acid is a secondary process.

Professor Smithells (Trans., 1892, **61**, 204, and 1894, **65**, 603) has recently shown that in the ordinary flame of cyanogen burning in air, the inner red cone corresponds with the combustion of the cyanogen to carbonic oxide, and the outer blue cone to the burning of this carbonic oxide to carbonic acid, results which are most easily explained on the supposition that in the ordinary flame of cyanogen the carbon is oxidised in two stages, the first product being carbonic oxide which is subsequently burnt to carbonic acid.

What is the nature of this secondary reaction?

We know that steam has a marked influence on the burning of carbonic oxide. An ordinary spark does not kindle a dried mixture of carbonic oxide and oxygen; a jet of dried carbonic oxide burning

* The combination would not be limited by dissociation at a high temperature, for carbonic acid is not dissociated into carbon and oxygen, but into carbonic oxide and oxygen.

in the air is extinguished by drying the air round it; the velocity of explosion of carbonic oxide and oxygen is increased by adding steam up to 5 per cent. of the volume of mixed gases. On the other hand, a heated platinum wire brings about the rapid union of dried carbonic oxide and oxygen; an electric spark causes the dried gases to combine in the heated region, but no flame is propagated in either case. By gradually separating the two cones of a cyanogen-air flame, Professor Smithells has found that a point may be reached where the carbonic oxide formed in the inner cone is no longer able to burn in the outer cone in the absence of steam; but, when the two cones are near together, the heated carbonic oxide burns in air, although all the gases have been carefully dried.

Beketoff (*Bull. Acad. St. Pétersbourg*, [2], 2, 175) has shown that the addition of some 10 per cent. of cyanogen to a dried mixture of carbonic oxide and oxygen causes the previously inert mixture to explode on the passage of a spark. It would seem, therefore, that dried carbonic oxide and oxygen do not unite directly with flame under ordinary circumstances, but when they are heated by wire or spark or previous chemical action, they are capable of rapid union, but not, apparently, of such a kind as takes place in, and causes the propagation of, the explosion-wave.

The Rate of Explosion of Cyanogen and Oxygen with Varying Quantities of Oxygen and Nitrogen.

The first point we investigated was the effect of excess of oxygen on the velocity of the "explosion-wave" of cyanogen. In the *Phil. Trans.*, 1893, it was shown that when cyanogen was exploded with its own volume of oxygen, and when nitrogen was added to the mixture, the rate of explosion could be calculated from a simple formula expressing the velocity of sound in the reacting gases before any loss of heat takes place. When oxygen was added to the mixture instead of nitrogen, the explosion was retarded to a greater extent, as sound would be if the heavier oxygen were as chemically inert as the lighter nitrogen; but it was found that, with successive additions of oxygen, the retardation did not increase *pari passu*, a fact which indicates that the formation of carbonic acid, although without influence on the velocity of the wave-front in the faster explosions, begins to exert an influence in the slower explosions. In the following table, the mean rates of explosion found are compared with those calculated from the formula

$$\Sigma = 0.7 \times 29.354 \sqrt{\frac{2 \left\{ \frac{Q}{S_v} + T \right\} \left\{ \frac{V_2}{V_1} \right\}^{\gamma-1}}{d}},$$

where Σ is the velocity of the explosion-wave in metres per second.*

Q is the heat disengaged by the reaction.

S_v is the molecular specific heat of the products of combustion at constant volume.

V_2/V_1 is the ratio of the volume of the products of combustion to the initial volume of gases, both being measured under the same conditions.†

T is the absolute temperature at which the gases are before the explosion, *e.g.*, $T = 286^\circ$ for experiments at 13°C .

γ is the ratio of the two specific heats.

d is the mean density of the unburnt and of the burnt gases (under the same conditions) referred to air.

The Rate of Explosion of Cyanogen Mixtures compared with the calculated Velocity of Sound, Σ .

1. *Cyanogen with Oxygen and Nitrogen.*

Mixture.	$\text{C}_2\text{N}_2 + \text{O}_2$.	$\text{C}_2\text{N}_2 + \text{O}_2 + \text{N}_2$.	$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$.
Rate of explosion	2728	2397	2163
Σ	2725	2397	2166

2. *Cyanogen with Oxygen.*

Mixture.	$\text{C}_2\text{N}_2 + \text{O}_2$.	$\text{C}_2\text{N}_2 + 2\text{O}_2$.	$\text{C}_2\text{N}_2 + 3\text{O}_2$.
Rate of explosion	2728	2321	2110
Σ	2725	2310	2066

The empirical formula, which expresses the rate of explosion of cyanogen with its own volume of oxygen, also expresses the rates of explosion when the mixture is diluted with one and with two volumes of nitrogen; but when the mixture is diluted with oxygen, the rate found gradually diverges from the rate calculated on the supposition that the cyanogen burns to carbonic oxide only. In order to make

* The formula gives approximately the velocity of sound in a medium having a temperature and density such as we suppose exist in the layer of reacting gases in which the wave is propagated. It is 2 per cent. faster than the velocity of sound calculated by the ordinary formula.

† This ratio, by a printer's error, is reversed in *Phil. Trans.*, *loc. cit.*, p. 133.

sure that this divergence was not due to experimental error, we have determined the rate of explosion of cyanogen with a still larger admixture of oxygen.

The experiments were carried out in the manner described in the *Phil. Trans.* The gases were fired in a half-inch leaden tube, the flame being allowed to run several feet before the measurement of velocity was begun. Dried cyanogen, mixed with four times its volume of dried oxygen, detonated along the half-inch tube, but when the corresponding mixture $\text{C}_2\text{N}_2 + \text{O}_2 + 3\text{N}_2$ was sparked, the explosion was not propagated. Two concordant experiments gave the rate of explosion for the mixture $\text{C}_2\text{N}_2 + 4\text{O}_2$.

	I.	2018	metres per second.
	II.	2032	„ „
		<hr/>	
Mean ..		2025	„ „

Now the velocity of the sound wave calculated by the formula, which gives the correct rate when nitrogen is the inert gas, is 1925 metres per second. The rate of explosion is, therefore, 5 per cent. greater than the rate calculated on the assumption that the cyanogen only burns to carbonic oxide in the wave front. It would appear, therefore, that the formation of carbonic acid in the flame is a factor in the propagation of the cyanogen explosion when a large excess of oxygen is used. The effect of the gradual addition of oxygen is shown graphically in Fig. 1 (p. 764), where the continuous line is drawn through the rates of explosion found with increasing quantities of oxygen, and the dotted line is drawn through the "theoretical" rates.

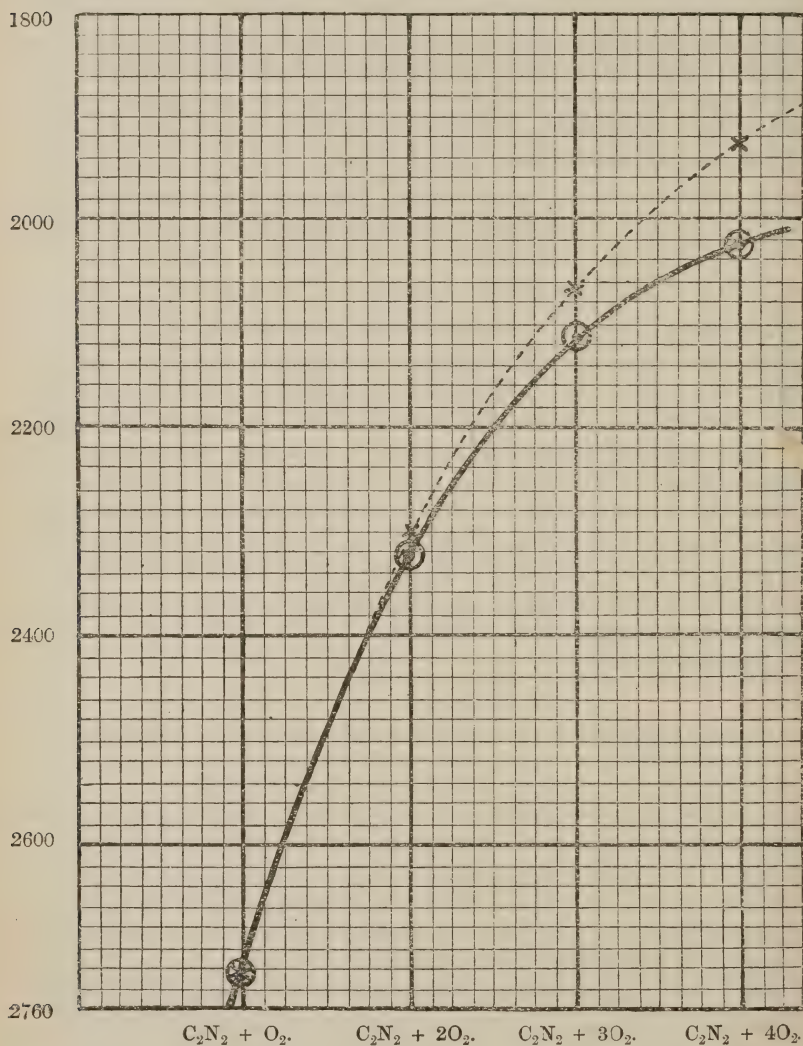
The Duration of the Flames produced by the Explosion of Cyanogen.

An attempt was made to study the intensity and duration of the flame following the explosion-wave of cyanogen and oxygen. Since the wave front travels much faster than sound in the unburnt mixture, the wave front must reach the end of a tube filled with the mixture before any other disturbance can be propagated through the gases to the end of the tube. If we imagine the pipe, along which the explosion-wave is propagated, to be closed by a thin diaphragm, the jet of flame which passes through the broken diaphragm is part of the column of burning gases following in the wake of the wave front; under similar conditions a long column of burning gases will produce a long jet of flame, and *vice versa*.

In practice it was found better to omit the diaphragm, and to place the explosive mixture in contact with an inert gas by turning a tap

between the two immediately before firing. The jets of flame were photographed on an iso-chromatic plate.

FIG. 1.—Curves showing the effect of the successive additions of oxygen on the rate of explosion of cyanogen.



The apparatus consisted of two tubes, one of lead, and the other of colourless glass, of the same internal diameter; they were joined together by a steel piece containing the tap, whose bore was the same as that



FIG. 2.—Jets of flame projected from tubes of different length filled with the mixture $C_2N_2 + 2O_2$.

Length of Firing-tube.—(i) 6 inches; (ii) $2\frac{1}{2}$ feet; (iii) $3\frac{1}{2}$ feet; (iv) 7 feet; (v) 13 feet.



FIG. 3.—Photographs of jets projected from a tube in which cyanogen is exploded, A to carbonic oxide, B to carbonic acid.

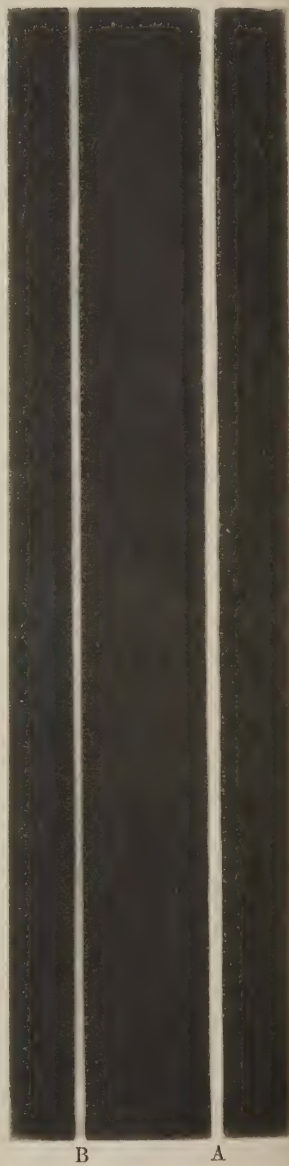


FIG. 4.—Photograph of the explosion of cyanogen, A to carbonic oxide, B to carbonic acid.

of the tubes. The steel piece carried a small side tube with tap, so that the leaden pipe could easily be filled with the explosive mixture from a mercury gas-holder. The glass tube was filled with a mixture of nitrogen and carbonic acid, of rather less specific gravity than the explosive gases. The whole was fixed vertically with the glass tube uppermost. By attaching a lever to the tap, the two tubes could be put into communication by the same motion that started a spark at the other end of the leaden pipe.

Preliminary photographs were taken to determine the length of the tube necessary to obtain a constant length of jet. Fig. 2 shows that when cyanogen is exploded with twice its volume of oxygen, the jet projected from the firing tube does not vary in length when the latter is over $3\frac{1}{2}$ ft. long. In the subsequent experiments, a tube about 4 ft. long was employed. The photographs show a remarkable constancy in the character of the flames ejected.

The dark lines crossing the images of the jets are due to narrow strips of paper gummed outside the glass tube, 1 ft. apart, the first being 1 ft. from the tap. The photographs do not directly tell us the length of the column of the luminous gases ejected, but only the furthest distance to which the jet was thrown.

The next figure (Fig. 3) shows the character of the jets produced by the burning of cyanogen to carbonic oxide and to carbonic acid respectively. The mixtures were fired in the same tube and under the same conditions, and the jets were photographed on the same plate.

The difference in the intensity and length of the jets is very striking. In comparing the two, it must be borne in mind that there is a large permanent expansion when cyanogen burns to carbonic oxide; when it burns to carbonic acid the mixture forms its own volume of permanent gases. If, therefore, the duration of the action were nearly the same in the two cases, we should expect the incomplete combustion to give the longer jet.

The relative luminous effect of the two explosions in closed tubes is shown in Fig. 4. The intensity of the light, as judged by the eye and by the effect on the photographic plate, is much brighter when cyanogen burns to carbonic oxide than when the combustion is complete. This agrees with the results of the pressure experiments made by M. Berthelot and with our own. The explosion of cyanogen to carbonic oxide is more violent in its disruptive effects than the explosion to carbonic acid.

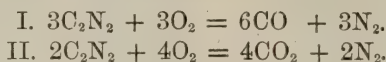
Fig. 4 is the direct photograph of two explosions (in the same tube and under the same conditions) taken on one plate. A is the explosion to carbonic oxide, B is the explosion to carbonic acid.

The next figure (Fig. 5) shows both the true explosion and the jet

in each case. A piece of clear glass tube was inserted in the leaden pipe below the steel tap. A shows the brilliant flash in the tube, and A' the feeble jet projected from the tube in the carbonic oxide explosion; B shows the less luminous flash in the carbonic acid explosion, and B' the jet of an intensity nearly equal to that of the explosion itself.

It is evident from these experiments that when cyanogen burns to carbonic oxide, the light of the explosion is more intense than when the combustion is complete, and that in the first case the column of burning gases behind the wave front gives comparatively little light, while in the second case the column of gases behind the wave front has nearly the same luminous effect as the explosion itself.

It is important to bear in mind the heat evolved and the temperature produced by the two reactions. In a tube filled with the two mixtures, under the same conditions, different amounts of cyanogen are burnt—according to the equations,



The total heat evolved in the first equation is

$$3Q_1 = 3 \times 126,100 \text{ cal.} = 378,300 \text{ cal.}$$

The total heat evolved in the second case is

$$2Q_2 = 2 \times 262,500 \text{ cal.} = 525,000 \text{ cal.}$$

If we assume that the specific heats of carbonic oxide and nitrogen remain constant at high temperatures, the mean temperature produced by the explosion to carbonic oxide is

$$T = \frac{Q}{S_v} = \frac{378,300}{4.8 \times 9}.$$

But, before expansion, 9 vols. of gas are condensed into the space previously occupied by 6 vols., so the temperature is increased by the heat due to this adiabatic compression. Assuming that the initial temperature of the gases was 13°C. or 286° on the absolute scale; the mean temperature produced by the explosion at constant volume would be $10,670^\circ \text{C.}$

With regard to the complete combustion, we may make two assumptions:

(a) The cyanogen burns to carbonic acid in the wave front. In this case, if the specific heats remain constant, the mean temperature is given by the equation:

$$T = \frac{Q}{S_v} = \frac{525,000}{(7.2 \times 4) + (4.8 \times 2)}.$$

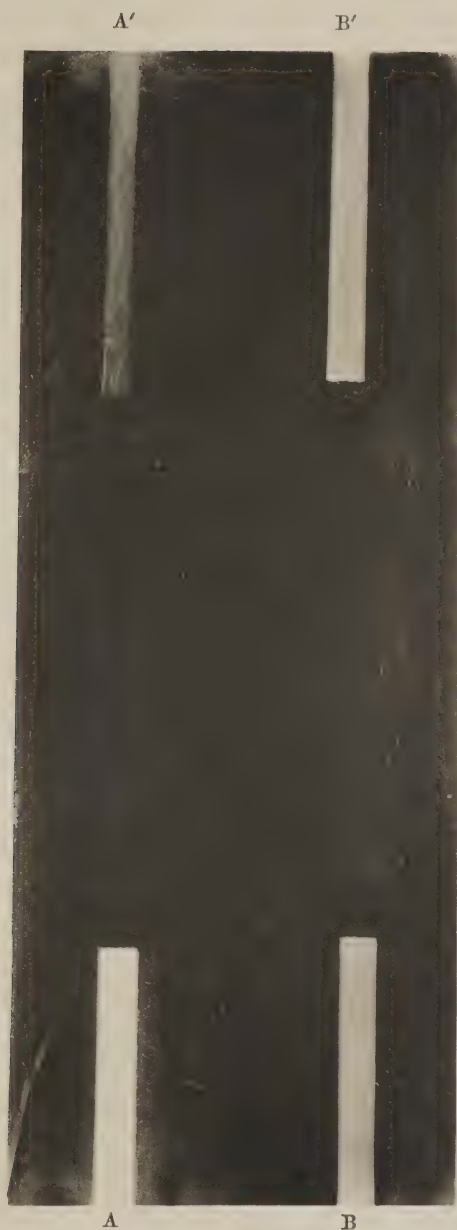


FIG. 5.—Photograph of the explosion of cyanogen and of the jet projected from the tube. A is the true explosion, A' the jet, burning to carbonic oxide; B the true explosion, B' the jet, burning to carbonic acid.

The mean temperature of the gases at constant volume would, therefore, be $13,674^{\circ}\text{C}$.

(b) The cyanogen burns to carbonic oxide only in the wave front, and the excess of oxygen afterwards combines with this carbonic oxide. In this case the mean temperature produced by the initial reaction, $\text{C}_2\text{N}_2 + 2\text{O}_2 = 2\text{CO} + \text{N}_2 + \text{O}_2$, would be, calculated as before, $7,707^{\circ}\text{C}$. But according to this assumption, the heated carbonic oxide and oxygen molecules combine behind the wave front maintaining a high temperature for a period more or less prolonged.

The phenomena brought to light by the photographs are readily accounted for by the second assumption. If the extra oxygen is inert in the wave front, it accounts for the superior brilliancy of the *unimpeded* reaction, $\text{C}_2\text{N}_2 + \text{O}_2 = 2\text{CO} + \text{N}_2$, over the *impeded* reaction, $\text{C}_2\text{N}_2 + 2\text{O}_2 = 2\text{CO} + \text{N}_2 + \text{O}_2$. If the formation of carbonic acid is a secondary action, taking place after the formation of the carbonic oxide, it accounts for the intensity of the jet of still uniting gases thrown from the tube after the wave front has traversed the explosive mixture.* On the other hand, it is not easy to reconcile the photographs with the assumption that carbonic acid is formed in the wave front: to say that the carbonic acid is dissociated is the same as to say that the carbonic oxide and oxygen do not unite in the wave.

Photographing the Explosion-flame on a rapidly moving Film.

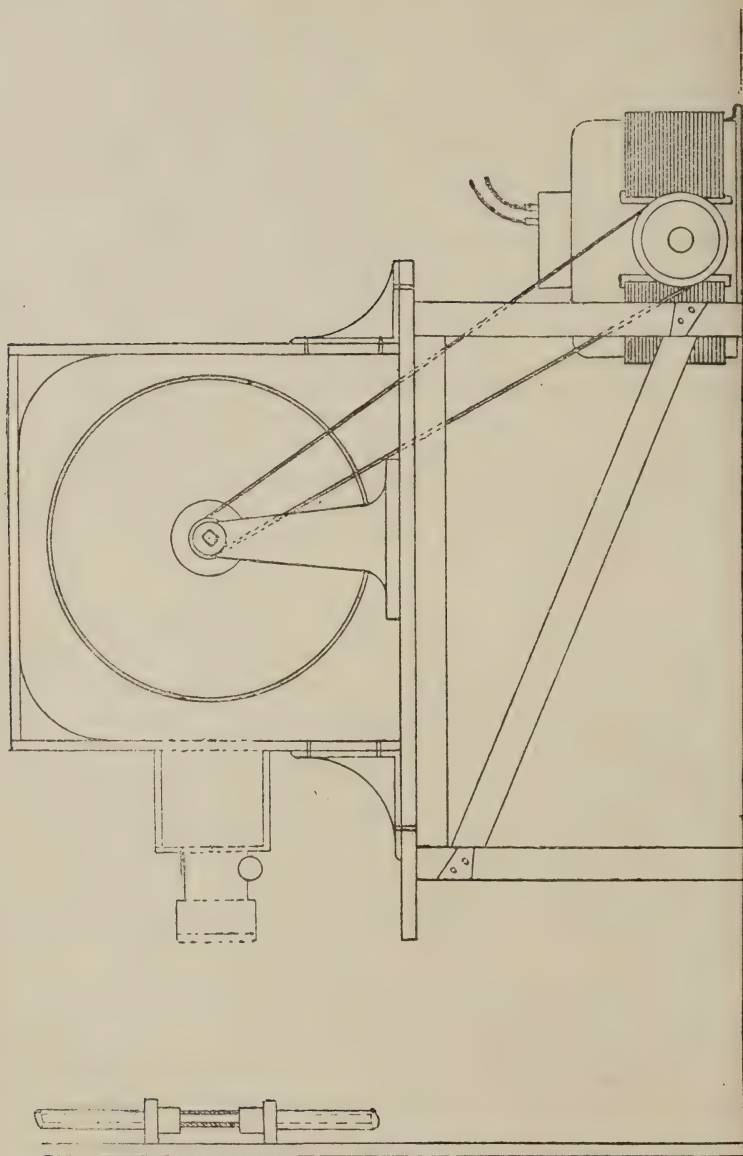
The problem of observing the real character of the explosion-flame of a detonating mixture of gases is one not easily solved. If the indirect observations recorded above are rightly interpreted, it would seem that the flame of cyanogen burning to carbonic oxide must be short and intense, and the flame of cyanogen burning to carbonic acid must be more prolonged and less intense. To obtain a direct record of the intensity and length of flame in the two cases we arranged an apparatus to photograph, on a very rapidly moving film, the passage of the explosion-flame through a short piece of glass tubing inserted in a long leaden pipe containing the explosive mixture.

A light iron drum, turning on hardened steel bearings, was fixed to a solid table clamped to the floor of the dark room (Fig. 6, p. 768). Round the edge of the drum, which was 94 cm. in circumference, a strip of sensitive celluloid film (Eastman's) was fastened. The drum was geared to a high-speed electric motor worked by a battery

* In the experiments with the open tubes the gases do work against the atmosphere by expanding; but this expansion only begins after the wave has gone by. Experiments have shown that the wave is just as brilliant and exerts the same breaking pressure whether it is traversing an open or a closed tube.

of secondary cells. The maximum speed attainable was 5,000 revolutions per minute. At this speed fairly sharp photographs of the

FIG. 6.



flame were obtained. As, however, the images of the longer flames were so drawn out at this velocity as to overlap round the film, a

slower speed was employed, usually about 1,500 metres per minute; at this speed there was very little vibration of the drum. The drum was enclosed in a camera holding a portrait lens with an aperture $\frac{f}{2.5}$. In order to determine the speed of revolution of the drum at the moment of firing, the flame itself was made to register the rate on the photographic film. The leaden pipe with the short glass "window" was bent round on itself, and a second window was inserted in a line with the first, the length of the tube between the two windows being accurately measured. On firing the gases in the pipe the flame first passed one window and then the second, at an interval of time depending on the rate of the explosion-wave and the distance between the two windows. If the drum were stationary the images of the two windows appeared side by side on the film, if the drum were rotating the images no longer appeared side by side, and the amount of the displacement readily gave the velocity of rotation, since the velocity of the explosion-wave in the mixtures used had previously been determined.

In many of the earlier photographs taken, curious irregularities in the intensity of the drawn-out images were observed. Some of these were found to be due to reflections from the end of the tube, and were eliminated by lengthening the pipe on each side of the window. Similar irregularities are shown in the photographs of the hydrogen and oxygen explosion taken by v. Oettingen and v. Gernet (*Ann. Phys. Chem.*, 1888, **33**, 586), and are no doubt due to interference-waves from the two ends of the tube. But we were long puzzled by certain wave-like variations in intensity, which were constantly reproduced. These, however, disappeared on changing the tube, and were then found to be due to an unsuspected constriction in the pipe we had been using.*

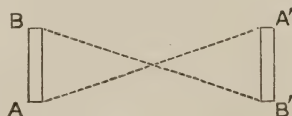
In the apparatus finally adopted, the flame traversed a leaden tube about 4 metres long from the firing-spark to the first window. This window consisted of a short piece of colourless glass tube let into two sockets in the two leaden pipes, so that the bore of the tube was the same in the lead and in the glass. The second leaden tube, of 2 metres in length, was curved round to the second window, which was exactly similar to the first. After passing the second window the flame traversed another leaden pipe 4 metres in length. A second firing tube was similarly arranged with its window in line with the two others. One tube was filled with cyanogen mixed with an equal volume of oxygen, the other with cyanogen mixed with twice its volume of oxygen. The wires being connected up in one

* We are attempting to measure the velocity of sound in burning gases by photographing these reflected waves.

circuit, the mixtures could be lighted simultaneously in the two tubes. Three images were thus obtained on the moving film, two were formed by one flame as it successively passed the two windows in the bent tube, the third was formed by the flame of the other explosive mixture as it passed its window. The windows were carefully shielded from one another by pieces of black velvet placed between them. By developing the film in a long trough in a uniform manner, the images of the several explosions received precisely the same treatment, and could be compared one with the other. In a successful experiment, the two images formed by the same mixture, as the flame passed in turn the two windows, were similar in character and nearly identical in intensity and length. This similarity afforded a proof of the uniformity of the film and of the development.

An examination of the photographs showed that the front of the flame in all cases was sharply defined, and that the whole diameter of the tube was illuminated at the same instant. There is therefore a definite front to the explosion-wave. When cyanogen is exploded with its own volume of oxygen, the image attains its maximum intensity apparently at once. This shows that the column of very highly heated gases must be very short.

FIG. 7.



Let AB represent the window along which the explosion passes upwards from A to B . Let $A'B'$ represent the image of the window on the film, the image of the explosion will pass downwards from A' to B' , and let the film itself be moving upwards with a velocity 100 times less than that of the flame (as is roughly the case). Now, if the flame were a horizontal line of light without breadth, the image would be equally illuminated from A' to B' . The motion of the film, being opposite to that of the image, would have drawn out the image by 1 per cent. Conversely, if the film were moving in the same direction as the image, the latter would be contracted by 1 per cent. Next suppose the flame not to be a line, but to be a column of uniform brightness equal in depth to the length of the window. When the wave front reaches A , the film at A' will be illuminated; but by the time the rear of the column reaches A its image will no longer fall on A' , for that point will have moved upwards a distance equal to $1/100$ th of the length of the image, and consequently the image will not attain its maximum intensity for the first hundredth

part of its length. From the abruptness with which the image attains its maximum intensity we may conclude that the length of the column of intensely ignited gases, in the case of cyanogen burning with its own volume of oxygen, is not greatly longer than the length of the window. On the other hand, when cyanogen is exploded with twice its volume of oxygen the image does not attain its maximum intensity at once.

The rear of the explosion-flame is in marked contrast to the front of the wave. In all cases it dies away with a tail which gradually thins out, and is similar in character to the jet of ignited gases thrown out from a tube filled with explosive gases. From the length of the tail, we can calculate the time during which the window was photographically luminous.

When cyanogen is exploded with its own volume of oxygen, the image shows an abrupt fall in intensity before the commencement of the tail. There is, in fact, an intense image of the window, only slightly drawn out by the revolution of the film, followed by a faint and short tail. From the shortness of the intense portion of the image, we also conclude that the length of the column of intensely ignited gases must be short.

But the length of the tail shows that a faint luminosity existed in the tube behind the wave front for a considerable time. Taking the average of the most concordant experiments, we find that the wave front must have travelled forward nearly 3 metres before this luminosity in the window ceased to affect the film.*

When, however, cyanogen is exploded with twice its volume of oxygen, the image is not so bright, and there is no abrupt fall in intensity; the image slowly and regularly diminishes in brightness to the end of the tail. The length of time during which the window remains fairly illuminated is far longer. Taking the average of several experiments, we find that the image of cyanogen burning to carbonic acid is drawn out to four and five times the length of the image of cyanogen burning to carbonic oxide. This increase in length cannot be due to dust or carbon particles, both of which are more likely to affect the more violent incomplete combustion, it must therefore depend on the longer period during which the gases are luminous.

At the suggestion of Professor Schuster, we made some experi-

* Besides the main reaction, the burning of the cyanogen to carbonic oxide, a slight liberation of free carbon takes place. This may be due to the dissociation of the heated carbonic oxide into carbon and carbonic acid. This carbon no doubt contributes to the luminosity of the "tail," and the effect of fine particles knocked from the sides of the tube and raised to incandescence would also be to prolong the illumination.

ments to determine whether the luminosity in the tail might be due to phosphorescence of oxygen. On photographing the explosion-flames of hydrogen (i) with its own volume of oxygen, and (ii) with half its volume of oxygen and half its volume of nitrogen, we found that the former mixture gives the shorter tail. The length of tail therefore does not depend on the phosphorescence of the oxygen left unburnt.

A comparison of the three images on the moving film (Fig. 8) brings out clearly the following points:—

(i) The burning of cyanogen to carbonic oxide produces the most brilliant flame (B).

(ii) The burning of cyanogen with twice its volume of oxygen produces a flame of the same initial intensity as when nitrogen is substituted for the second volume of oxygen (C and D).

(iii) The tail of the flame in B is short, and of feeble intensity.

(iv) The tail of the flame when cyanogen burns with excess of oxygen is long, and its luminosity falls very gradually (D).

(v) When cyanogen burns to carbonic oxide in presence of nitrogen, the tail is of feeble intensity, but longer than in the absence of the inert gas (C).

The results of these experiments seem to us to agree entirely with the results obtained by photographing the "jets"; and are most readily explained on the supposition that the formation of carbonic acid is mainly due to a secondary action between the heated carbonic oxide and oxygen left in the rear of the explosion-wave. The nature of the flame produced when cyanogen is exploded with oxygen thus supports the hypothesis which had previously been arrived at from the velocity of the explosion-wave.

We have also examined by this method the length of flame produced by other explosive mixtures, *e.g.*, that of hydrogen and oxygen, carbonic oxide and oxygen. They exhibit the same characteristic sharpness of wave front and gradual fading of luminosity in the tail. In the case of hydrogen and oxygen, the gas is still luminous when the wave front has travelled forward some 15 metres. This "tail" is greatly diminished in length when the electrolytic gas is mixed with an excess of hydrogen.* In his experiments on the electrical conduction of the flame produced by the explosion of hydrogen and oxygen, Dr. Turpin† found that the wave front had moved forward about 2 metres, on the average, before the column of gases ceased to conduct, but with excess of hydrogen the flame was shorter.

* We are now studying the oxy-hydrogen and other flames by this method in greater detail.

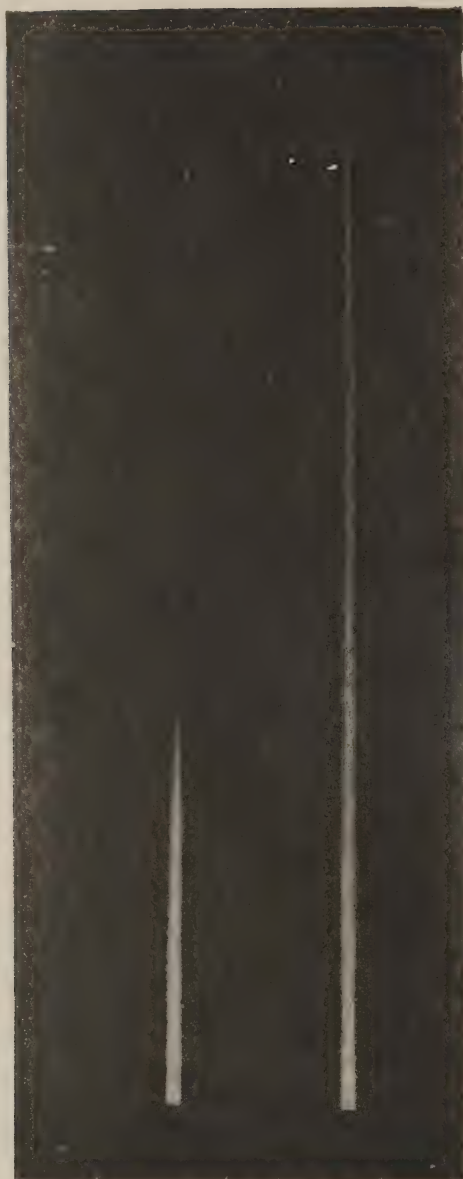
† *Studies from the Physical and Chemical Laboratories of the Owens College* (1893), p. 295.



D C B A

FIG. 8.—Photographs of the explosion of cyanogen and oxygen passing a window in a long tube.

- A. Explosion of $C_2N_2 + O_2$ taken on stationary film.
- B. Explosion of $C_2N_2 + O_2$ taken on moving film.
- C. Explosion of $C_2N_2 + O_2 + N_2$ taken on moving film.
- D. Explosion of $C_2N_2 + 2O_2$ taken on moving film.



A

B

FIG. 9.

- A. The explosion of moist carbonic oxide and oxygen.
B. The explosion of dried carbonic oxide and oxygen.

The Effect of Steam on the Burning of Cyanogen to Carbonic acid.

Considering the effect produced by the presence of steam on the explosion of a mixture of carbonic oxide and oxygen, it might be conjectured that when cyanogen is burnt to carbonic acid the presence of steam might materially affect the rate of combination, and consequently the length of the flame. But the flame produced by a well dried mixture of cyanogen and oxygen does not appear to differ from the flame given by the same gases mixed with 1.5 per cent. of steam. This result, which was contrary to our expectations, was shown by a series of photographs of the flames produced by the explosion of the dried and wet mixtures under similar conditions. As before, two tubes, furnished with similar windows, were fixed side by side. After thoroughly drying one tube, we filled it with the mixture which had been standing some days over phosphoric oxide. The second tube was filled with gas nearly saturated with steam. The mixtures were fired at the same time, and the flames on reaching the windows in the two tubes were photographed on the moving film. Both with slow and high velocities of the film, the images were drawn out equally. We can only conclude from this result that, in a mixture of freshly formed carbonic oxide and oxygen, these gases unite as the mass cools down without the intervention of steam; and where steam is present it does not appreciably alter the time during which the change continues.

This result agrees with Professor Smithells' observation that when a dried mixture of cyanogen and air is burnt in his "separator," the carbonic oxide formed in the inner cone will burn in dry air, provided the outer cone is kept close to the inner; but when the cones are widely separated, so as to allow time for the carbonic oxide formed below to "settle down," the outer flame is extinguished on bringing it into dry air.

The Effect of Steam on the Flame of Carbonic Oxide and Oxygen.

Experiments similar to the above, made with the tubes filled with dried and moist carbonic oxide and oxygen respectively, show a marked difference (Fig. 9). In the presence of steam, the flame is much shorter. In the dried mixture, the gases were passed through several tubes containing boiled sulphuric acid, and through a column of phosphoric oxide. Care had to be taken to allow the flame a long run before reaching the window, as in the dried gases the explosion-wave is not set up for several feet. The photographs of the carbonic oxide flame thus seem to bear out the hypothesis, founded on the rates of explosion, that "at the extreme temperatures

of the explosion-wave, as well as in ordinary combustion, carbonic oxide is oxidised by the steam" (*Phil. Trans.*, 1893, 184, 112).

A considerable body of evidence has now been accumulated concerning the mode of burning of cyanogen. The principal points established are:—

(i) Cyanogen burns and explodes with oxygen in the absence of moisture.

(ii) Cyanogen in explosions forms carbonic oxide with great rapidity, and carbonic acid with less rapidity.

(iii) Cyanogen, burning in air, appears to undergo oxidation in two stages.

(iv) The presence of moisture does not affect the formation of carbonic acid from freshly formed carbonic oxide.

If we have rightly interpreted the facts before us, it would appear that cyanogen, in explosions, burns first to carbonic oxide, and then, if oxygen is present, this carbonic oxide proceeds to unite with it to form carbonic acid. This formation of carbonic acid is slow compared with the formation of the carbonic oxide; nevertheless, the reaction is rapid enough to influence the velocity of explosion of cyanogen with a large excess of oxygen.

Owens College,
Manchester.

XLVI.—*The Mode of Formation of Carbonic acid in the burning of Carbon Compounds.*

By Professor HAROLD BAILY DIXON, M.A., F.R.S.

THE usual statements concerning the burning of carbon compounds, namely, that the carbon unites directly with oxygen to form carbonic acid, and that this is reduced in presence of an excess of the carbon to carbonic oxide, appear to have little or no experimental foundation. All the direct evidence points the other way.

But with regard to the mode in which carbonic acid is formed, and the part played by moisture in its formation, the evidence is curiously puzzling. Granting that carbon in any compound may burn with oxygen to carbonic oxide, we have to deal with the following facts:—

1. An explosion is not propagated by a spark in a dried mixture of carbonic oxide and oxygen at ordinary temperature and pressure (Dixon, *Brit. Assoc. Report*, 1880, 503).

2. When a long tube full of the dried gases has moisture introduced at one end and the gases are ignited there, the flame traverses

the moist gases, but dies out on reaching the dry gases (Dixon, *Chem. News*, 1882, **46**, 151). The flame of dry carbonic oxide burning in air is extinguished by plunging it into dry air (M. Traube, *Ber.*, 1885, *b*, 1890).

3. The addition of steam increases the rapidity of inflammation of carbonic oxide and oxygen, both in the ordinary flame and in the explosion-wave (Dixon, *Phil. Trans.*, 1884, Pt. 2, 640, and 1893, A, 111).

4. Carbonic oxide and oxygen appear to be inert towards one another in the incomplete combustion of hydrogen and carbonic oxide; at all events, they act as if they were incapable of rapidly uniting (Dixon, *Phil. Trans.*, 1884, Pt. 2, 671).

5. Dried carbon does not glow when heated in dried oxygen; it burns, however, to carbonic oxide. In the presence of finely divided platinum, carbonic acid is formed (Baker, *Phil. Trans.*, 1888, A, 571).

6. Dried carbonic oxide and oxygen will unite in the path of the electric spark (Lothar Meyer, *Ber.*, 1886, **19**, 1099; Beketoff, *Bull. Acad. St. Pétersbourg*, [N.S.], **2**, 175; Dixon). The amount of combination depends upon the nature of the spark; a limit is reached when the rate of combination is equal to the rate of decomposition of the carbonic acid formed (Dixon and Lowe, *Trans.*, 1885, 571).

7. The dried gases completely combine, without producing flame, in contact with a heated platinum wire (Dixon and Lowe, *Trans.*, 1885, 576).

8. Dry carbonic oxide proceeding from a half-burnt cyanogen flame will burn in dried air, provided the two flames are close together (Smithells and Dent, *Trans.*, 1894, 603).

9. An explosion of cyanogen and oxygen will cause the union of dry carbonic oxide and oxygen with which they are mixed (Beketoff, *Bull. Acad. St. Pétersbourg*, [N.S.], **2**, 175).

10. In the explosion of cyanogen with an excess of oxygen, the formation of carbonic acid is complete, and is not affected by the presence of moisture (Dixon, *Trans.*, 1886, 384). The complete combustion of cyanogen, however, does not take place so rapidly or with such violence as the incomplete combustion to carbonic oxide (Dixon, Strange, and Graham, *Trans.*, 1896).

11. Moisture is active in the oxidation of other substances, *e.g.*, sulphur and phosphorus (Baker, *Phil. Trans.*, 1888, A, 581); it also affects the combination of other substances (Cowper,* *Trans.*, 1883, 153; Baker, *Trans.*, 1894, 611; Pringsheim, *Ann. Phys. u. Chem.*,

* The effect of moisture in determining the combination of chlorine and sodium, the discovery of which is usually attributed to Wanklyn, is not mentioned by Wanklyn in his paper (*Chem. News*, **20**, 271).

[N.F.], **32**, 384), and facilitates the passage of the electric discharge in gases (J. J. Thomson, *Phil. Mag.*, [5], **36**, 313; *Brit. Assoc. Report*, 1894, 482).

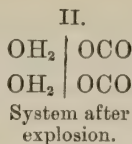
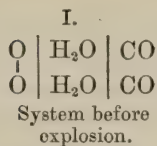
Several explanations have been put forward to account for the influence of moisture in promoting the combination of carbonic oxide and oxygen; some of these have special reference to this reaction only, whilst others are of more general application. Most of the hypotheses advanced have, on examination, suggested experiments by which their probability might be tested. It will, I think, be useful to examine these hypotheses in the light of the evidence which has been accumulated. Even if it should appear, as I think, that no satisfactory explanation has been arrived at, a discussion of the results may focus attention on the essential points of the problem, and may serve to suggest future experiments.

In my papers on the subject I have made no attempt to suggest a reason why oxygen should not explode with carbonic oxide. I have limited myself to the conclusions which seemed to accord most closely with the observations: (a) that carbon burns primarily to carbonic oxide; (b) that carbonic oxide is inert, under ordinary conditions, towards oxygen; and (c) that carbonic oxide at a high temperature decomposes steam to form carbonic acid and hydrogen, so that, in the ordinary explosion of moist carbonic oxide and oxygen, the steam acts catalytically as a carrier of oxygen.

It is evident, from the results recorded in the previous paper on "The Explosion of Cyanogen," that the second conclusion (b) must be modified. Under certain conditions, carbonic oxide and oxygen unite readily. We are confronted, therefore, with the apparent anomaly—two gases which are not exploded by the spark or application of a flame, which are inert, or do not unite rapidly, as other gases do, in explosions, nevertheless combine in presence of heated platinum, and in presence of other combining gases, or if one of them has just been formed by a chemical reaction.

Professor H. E. Armstrong,* taking a wide survey of the conditions of chemical combination, considers the function of the steam in the explosion of carbonic oxide and oxygen to be that of the liquid in a galvanic cell. The two gases, inert in the pure state, require "the formation of a conducting system in which electrolysis can occur." Comparing the system of carbonic oxide, steam, and oxygen to a Grove gas battery, Armstrong regards the oxidation of the carbonic oxide by the oxygen of the water as dependent upon the simultaneous oxidation of the hydrogen of the water by the free oxygen.

* "Presidential Address to Chemical Section, British Association, 1885," *Proc. Roy. Soc.*, 1886, **40**, 287; *Trans.*, 1886, **49**, 112. "Presidential Address to Chemical Society," *Trans.*, 1895.



The general theory advocated by Armstrong is that interaction does not occur between two pure substances, and that water will condition the interaction between them only if it be capable of forming a composite electrolyte with one of them. I am not sure whether Armstrong considers that water forms a composite electrolyte with carbonic oxide, or whether water itself is the electrolyte; but, in either case, it is not easy to explain all the facts. The theory, as I understand it, supposes that the three substances, carbonic oxide, steam, and oxygen must be in contact while the change proceeds, and any two of these gases will be inert on meeting. If, therefore, we accept the molecular theory of gases, the change will only occur on the simultaneous collision of molecules of the three substances; or, taking Armstrong's equation, on the simultaneous collision of five particular molecules, two of carbonic oxide, two of steam, and one of oxygen. What the chances are in favour of such collisions occurring might, I suppose, be calculated; it is obvious that their number must be exceedingly small, compared with the collisions between any two molecules. Supposing this quintuple collision occurred, the heat evolved by the chemical change would be divided among the products of interaction; the heated steam and carbonic acid molecules so formed would fly in all directions, and inevitably some steam molecules would come into violent collision with unburnt carbonic oxide molecules. What would happen? Experiment shows that if we heat carbonic oxide and steam together, they react, forming carbonic acid and hydrogen. Do they do so in the case supposed above? If they do, carbonic acid is formed in a manner independent of electrolytic conduction. If they do not, how are we to explain the action of heat on carbonic oxide and steam?

Again, the electrolyte theory has to explain the oxidation of carbonic oxide in the burning of cyanogen. As we have seen, moisture does not appear to be necessary for this reaction or to appreciably affect the result if present. I have tried an experiment to see whether some oxide of nitrogen, which might be formed in the initial combustion of the cyanogen, can act the part of "catalyst" between carbonic oxide and oxygen. Peroxide of nitrogen I found to have no effect; nitrous oxide I had previously tried with the same result.

But apart from these difficulties, we must bear in mind that an explosion in moist carbonic oxide and oxygen is propagated at a

velocity of over 1700 metres per second. This velocity of explosion, though inferior to that of hydrogen and oxygen, is comparable with that of hydrogen and chlorine, an explosive mixture in which the flame is propagated though the gases be carefully dried. The rate of the explosive wave in gases approximates, according to M. Berthelot's theory, to the mean rate of movement of the products of combustion before they have lost any heat, or, according to my hypothesis, to the velocity of sound in the burning gases, which is equal to the mean rate of the *forward* movement of the reacting molecules.

Without insisting on the exactness of these theories, we may ask whether it is more probable that the flame is propagated at such velocities from molecule to molecule, or whether the flame can only advance as simultaneous collisions occur of five particular molecules out of three sets? In our present state of knowledge, I believe the former view presents far fewer difficulties, and accordingly I think we are not yet warranted in applying the electrolytic theory to explain the reactions of gases *at high temperatures*.

Professor J. J. Thomson, who has made experiments of remarkable interest on the electrolysis of gases, has given us a theory as to the function of water in the explosion of carbonic oxide and oxygen. Finding that the presence of a trace of aqueous vapour in a gas greatly facilitates the passage of the electric discharge, and permits a phosphorescent glow to be formed in the gas after the discharge has passed, Thomson compares these phenomena with the effects of moisture on chemical combination. If the first discharge through a gas is accompanied by a splitting up of some of the molecules we can see, he says, "why a cause which increases the facility with which the first discharge passes through the gas should also increase the tendency of the gas to enter into chemical combination." The theory, as I understand it, is this: Pure water, though not a conductor, has such a high specific inductive capacity that its electrostatic effect is much the same as if it were a conductor. A molecule of two oppositely charged atoms, coming close to the sphere of liquid water, might be disassociated owing to the power which the atoms would possess of unopposed movement along the surface of the sphere. Such separated atoms would be more ready to enter into chemical combination than the undecomposed molecule.

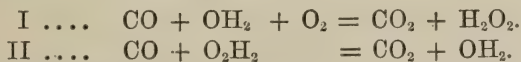
In order that this dissociation of molecules should be brought about, the presence of drops of liquid water is necessary. They might be condensed only for an instant and then evaporate. This formation of transitory drops of water is to be expected, Thomson says, even when the vapour is far below saturation. But to explain the combination of carbonic oxide and oxygen in the explosion-wave, a trace of steam far below saturation at ordinary temperatures would

have to be condensed into liquid particles at a temperature which has, I believe, never been estimated below 3000°C. , and is probably very much higher. But perhaps I have misunderstood Thomson's meaning. Should it be supposed that the vapour really does its work of dissociation in the unburnt gas, leaving, by alternate condensation and evaporation, loosely combined atoms of oxygen which combine with carbonic oxide when the explosion reaches them? According to this view, the work of the moisture would be preparatory. But it must be remembered that a small quantity of hydrogen, or other inflammable gas, containing hydrogen, confers inflammability on the mixture. Now, this hydrogen only forms steam when the explosion reaches it; nevertheless, it enables the carbonic oxide to burn. In this case, the steam molecules must exert their influence in the flame itself, and not in the cool unburnt gas.

Thomson states that oxygen when carefully dried shows no phosphorescence after the discharge; air, on the other hand, is made phosphorescent by carefully drying. If this power of phosphorescing is connected with the dissociation of the atoms, as is suggested, we should expect carbonic oxide to burn in dry air. But experiment shows that the carbonic oxide flame is more readily extinguished in dry air than in dry oxygen.

But while I hold that the effect of moisture in transmitting an explosion in carbonic oxide and oxygen has not been shown to be due to an electrolytic or to a dissociating action on the part of the water, I believe these influences may be at work in the interaction of gases at ordinary temperatures,* such as have been studied more particularly by Brereton Baker. The influence of platinum in determining the union of dry carbonic oxide and oxygen may be due to the conductivity of the metal, or, on the other hand, to its attraction for oxygen. There is perhaps a danger lest in seeking for general laws we may miss some simpler explanation.

Moritz Traube (*Ber.*, 1885, *b*, 1890) in 1885 advanced the hypothesis that the function of the steam in the explosion is to yield its atom of oxygen to the carbonic oxide at the same time that its hydrogen unites with a molecule of oxygen to form hydrogen peroxide, and that the latter interacts with more carbonic oxide to reform steam and carbonic acid:—

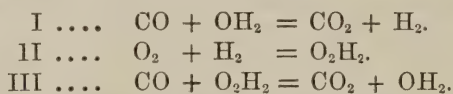


I have dealt fully with this hypothesis in a former communication

* I have shown that oxygen does not combine with sulphurous oxide in presence of steam at temperatures up to 100°C. ; in presence of particles of liquid water, oxidation takes place, *Journ. Gas Lighting*, 1881, **37**, 704.

to this Society (Trans., 1886, 49, 94), Since it was put forward mainly on the mistaken ground that carbonic oxide was not oxidised by steam at a high temperature, the refutation of this error removed the chief argument in its favour.

Mendeléeff (*Principles of Chemistry* (Eng. Ed.), 1891), rejecting Traube's first equation, considers that the carbonic oxide is oxidised directly by the steam, but thinks that the liberated hydrogen combines with a molecule of oxygen to form hydrogen peroxide, which in turn is reduced by more carbonic oxide.



This opinion is grounded on his conviction that gases enter into combination in equal volumes, and that the apparent exceptions to this law of nature are to be accounted for by supposing that such reactions are in reality complex, the initial reactions being between equal volumes. The law that *reactions of equal volumes precede all others* affords the simplest explanation, according to Mendeléeff, of the necessity for the presence of steam to bring about the union of carbonic oxide and oxygen, since the direct oxidation of carbonic oxide by oxygen would involve an action between unequal volumes of gases.

As an instance of the application of this law, we may glance at Mendeléeff's suggestion that the synthesis of ammonia takes place through the initial formation of N_2H_2 , which, in turn, unites with its own volume of hydrogen to form hydrazine, N_2H_4 , which finally breaks up into nitrogen and ammonia. Without discussing the general validity of the law which Mendeléeff here lays stress upon, it will be sufficient for my immediate purpose to refer to an experiment which I have made with carbonic oxide and nitrous oxide. These gases, mixed in equal volumes over mercury in the ordinary way, are readily exploded by a spark. According to Mendeléeff's view, there is nothing to prevent these gases, when dry, from interacting, since equal volumes are concerned. Actually, they resist the action of the spark when well dried; the addition of a trace of water renders them readily explosive again. The influence of steam does not appear, therefore, to be explained by the law of equal volumes.

The late Professor Lothar Meyer (*Ber.*, 1886, 19, 1099), who was one of the first to repeat the experiment with the dried gases, put forward the view that it was the high temperature required for the ignition of carbonic oxide and oxygen—compared with the temperature at which carbonic oxide reacts with steam—that favoured the

combination of the moist gases. If a very high temperature were required for the ignition of carbonic oxide and oxygen, and a lower temperature for the action between carbonic oxide and steam, the latter would occur with greater readiness in the neighbourhood of the spark; and if the liberated hydrogen could combine with oxygen at a low temperature also, steam would be reformed and the process would be repeated by the alternate reduction and oxidation of steam. Adopting my view as to the course of the chemical changes occurring, Lothar Meyer explains them on the ground that the direct oxidation requires a far higher temperature than the indirect action; he found that a very powerful spark, driven lengthways through a column of dried carbonic oxide and oxygen, would bring about the union of the gases, and that in a stream of strong sparks complete combination took place in a short time. He attributes the combination to the very high temperature of the spark, which is not maintained except in the path of the discharge, and so the incipient explosion set up in the path dies out around it. In favour of this view, he quotes my own observations on the limits of dissociation of carbonic acid by the electric spark, and the combination of dried carbonic oxide and oxygen by heated platinum (*Trans.*, 1885, 571). With a feeble discharge, the dissociation of carbonic acid is greater than when the sparks are strong. Again, when a platinum wire is heated in a mixture of dried carbonic oxide and oxygen, the wire glows intensely, and complete combination takes place without flame on the surface of the platinum. The platinum, according to Lothar Meyer, supplies the heat necessary for direct combination.

Mallard and Le Chatelier (*Mélanges Gazeux explosifs*, 7, found the ignition point of hydrogen and oxygen to be about 550° , and that of carbonic oxide and oxygen to be about 650° . Victor Meyer and Freyer (*Zeit. physikal. Chem.*, 11, 28) found that the ignition point of hydrogen and oxygen, in a closed bulb, lay between 530° and 606° , whilst that of carbonic oxide and oxygen lay between 650° and 730° . On the other hand, Naumann and Pistor (*Ber.*, 18, 2894) found that carbonic oxide was not oxidised by steam below 600° , but oxidation began between 602° and 634° . These observations so far agree with Lothar Meyer's explanation that they show that carbonic oxide and oxygen do not explode until a temperature is reached at which the carbonic oxide could be oxidised by the steam present, and the liberated hydrogen could reform steam. But I think no satisfactory evidence has been adduced to show that it is merely owing to an insufficient temperature being reached that an explosion is not propagated in dry carbonic oxide and oxygen. At first sight, the results obtained in the explosion of cyanogen seem to favour Lothar Meyer's view; for the carbonic

oxide produced in the wave-front must be at a very high temperature, and it is found to combine with the oxygen present. Although, it might be argued, the explosion is not propagated in dry carbonic oxide and oxygen at ordinary temperatures, nevertheless, when these gases are mixed together in a very highly heated state, as they are in the combustion of cyanogen, then the two gases can unite explosively. But this is not really the case. If the carbonic oxide only required a high temperature to unite with oxygen, it should do so the moment after it is formed, for it is then at its maximum temperature. The immediate formation of carbonic acid should ensue from the collisions between oxygen molecules and the highly heated carbonic oxide molecules formed in the wave-front. Thus the complete combustion of cyanogen would be rapidly effected, and the temperature reached would be far higher than in the incomplete combustion. Now both the photographs of the flame and the rates of explosion show that this complete combustion does not take place immediately on the explosion of cyanogen; on the contrary, the extra oxygen appears to be inert in the wave-front, and only combines gradually behind the wave.

Again, if Lothar Meyer's view is correct, a considerable increase in temperature of one of the gases might be expected to increase the inflammability of carbonic oxide in air. As Traube first demonstrated, an ignited jet of carbonic oxide, dried by oil of vitriol, is extinguished on being plunged into a jar full of air dried in the same way; the flame is usually put out an inch or two from the mouth of the jar. The same result is found when the stream of carbonic oxide is strongly heated before it burns. The glass tube bringing the gas from the drying towers was luted by means of asbestos and soluble glass to a platinum tube 6 in. long. Round a length of 4 in. of the platinum an asbestos jacket was fitted, and the whole was heated strongly by two blow-pipe flames. At a bright red heat the blue colour of the carbonic oxide flame burning in the air at the mouth of the tube changed to a pinkish-orange. On plunging the flame into the jar full of dried air, it was extinguished quite as readily as it was without heating. On withdrawing the tube from the jar the gas immediately rekindled on meeting the ordinary air. The experiment was repeated several times with hot and cold gas alternately, and always with the same result. The high temperature of the carbonic oxide in no way increased its inflammability in dry air.

Apart, therefore, from the difficulty of understanding how a flame of burning carbonic oxide and oxygen, which has, at least, a mean temperature of 3000° , is extinguished in the dried gases, owing to the temperature not being high enough, or how the intensely heated carbonic oxide formed in the explosion of cyanogen does not burn in

the wave-front, whilst a red hot platinum wire is admittedly hot enough to bring about the combination, we have some direct evidence to show that the non-explosibility of carbonic oxide and oxygen is not simply a result of insufficient temperature.

M. Beketoff (*Bull. Acad. St. Pétersbourg*, [N.S.], 2, 175) has sparked a dried mixture of carbonic oxide and oxygen, and found that carbonic acid was gradually formed; he has also brought about the union of the dry gases by mixing 10 per cent. of cyanogen with them and then exploding. M. Beketoff's view of the function of the moisture is that it acts by reason of the ready dissociation of its molecule into hydrogen and an atom of oxygen which combines with the carbonic oxide. Steam begins to dissociate at 800° , he says, oxygen is stable at 2000° . "The molecules of steam furnish the atomic oxygen which is indispensable for the combustion of carbonic oxide more readily than the molecules of oxygen themselves." But of course this theory only puts off the difficulty one stage. If carbonic oxide has not the power to break up oxygen, why should the liberated hydrogen be able to do so? The heat of formation of carbonic acid from carbonic oxide is greater than the heat of formation of steam from hydrogen. M. Beketoff only leaves us with a greater difficulty to explain.

The experiment, made by M. Beketoff, of firing cyanogen and oxygen mixed with carbonic oxide and oxygen, in the dry state, is of considerable interest, since it shows that the burning of the cyanogen affects the union of the carbonic oxide with which it is in contact. He considers that this result is due to the high temperature produced by the burning cyanogen; this high temperature, he thinks, by breaking up the oxygen molecules causes the carbonic oxide to burn. M. Beketoff does not say that he analysed the residual gases; had he done so, he would probably have found that the combustion was not complete. Some years ago (in 1884), I tried the effect of mixing some carbon bisulphide vapour with carbonic oxide, and with enough oxygen to burn them both. After the gases had been well dried, a spark produced a flame which traversed the whole column of gases, but only caused a partial combustion of the carbonic oxide.

I have lately repeated these experiments, using different quantities of carbon bisulphide and cyanogen. Mixtures of carbon bisulphide with oxygen and with nitrous oxide sufficient for complete combustion were prepared and allowed to stand over mercury in contact with phosphoric oxide; a mixture of cyanogen with twice its volume of oxygen was also dried in the same way. Into tubes, containing some 40 c.c. of a mixture of carbonic oxide with oxygen or with nitrous oxide over mercury, phosphoric oxide was introduced, and the gases were allowed to dry for a week; they were then tested by

sparks.* Into several tubes containing the non-inflammable mixture, portions of the explosive mixtures were introduced, and the gases allowed to diffuse for 24 hours; a spark was then passed.

In the first experiment, a dried mixture of carbon bisulphide and nitrous oxide ($\text{CS}_2 + 6\text{N}_2\text{O}$) was added little by little to a dried mixture of carbonic oxide and nitrous oxide ($\text{CO} + \text{N}_2\text{O}$). When 17.6 per cent. of the carbon bisulphide mixture had been added, the gas did not inflame, but when 20 per cent. had been added, the spark produced a flame which traversed the tube. The carbon bisulphide formed 2.8 per cent. of the total mixture. After the absorption of sulphurous oxide by manganese peroxide, and of carbonic acid by potash, the residual gas exploded violently on passing a spark. The analysis showed that the combustion of the carbon bisulphide was not complete,† and over 90 per cent. of the original carbonic oxide had escaped combustion in the first explosion.

In a second experiment, the composition of the mixture was

CO	56
CS_2	4
O_2	40

After explosion, it was found that 13.8 per cent. of the original carbonic oxide was unburnt.

In a third experiment, the composition of the mixture was

CO	45
CS_2	8
O_2	47

The combustion was practically complete at the first explosion.

Two cyanogen mixtures were made. In the first experiment, the composition of the mixture was

CO	53.3
C_2N_2	6.7
O_2	40.0

* In two of the tubes so tested, the third or fourth spark set up a flame which traversed the whole column of gas, and appeared to linger some time at the bottom of the column where the phosphoric oxide was lying. The analysis of the gases showed that in one case 37 per cent., and in the other 50 per cent., of the carbonic oxide remained unburnt.

† The escape of some of the readily combustible CS_2 shows that an inflammable gas, together with an excess of oxygen, may pass through a flame.

Professor Smithells (Trans., 1894, 65, 608) found that some unburnt cyanogen passed through the inner cone of a cyanogen-air flame, although some carbonic acid was also being produced in the flame. I see no difficulty in the view that the cyanogen burns to CO in the inner cone, and this CO begins to be oxidised to CO_2 before all the cyanogen is burnt. The inner cone of the divided flame is burning at constant pressure; the conditions are wholly different from those of the explosion-wave.

that is, the cyanogen detonating gas formed 20 per cent. of the mixture. The spark produced an explosion in which the cyanogen was completely burnt, together with two-thirds of the carbonic oxide. After the absorption of the carbonic acid, the residual gases were exploded, when it was found that 32·3 per cent. of the original carbonic oxide had escaped combustion in the first explosion.

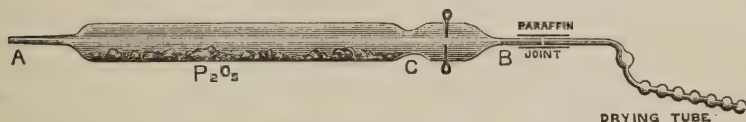
In the second experiment, the composition of the mixture was

CO	43·3
C ₂ N ₂	11·7
O ₂	45·0

that is, the cyanogen detonating gas formed 35 per cent. of the mixture. In the first explosion, 13 per cent. of the original carbonic oxide escaped combustion.

The chief results established by these experiments are—(i) that it is possible to submit the dried mixture of carbonic oxide and oxygen to the intimate contact of a flame without causing complete combustion, and (ii) that the quantity of carbonic oxide burnt depends upon the intensity of the exciting flame.

The opinion advanced by Lothar Meyer and by Beketoff that the dried mixture resists explosion owing to the stability of the oxygen molecule, led me to try the effect of the spark on a dried mixture of carbonic oxide with ozonised oxygen. Some difficulty was experienced in obtaining phosphoric oxide of sufficient purity not to act on the ozone.



The arrangement shown in the figure was finally adopted. The tube AB was constricted slightly at C and drawn out at B. Phosphoric oxide was placed along the tube from A to C, and the tube was then drawn out at A to a very fine point. The end B was connected by a paraffin joint to a long drying tube containing boiled sulphuric acid. A slow stream of oxygen was then sent through the apparatus while the tube was heated below redness in a gas furnace from A to C. The heating was maintained for four days in the stream of oxygen, after which a Siemens' induction tube was inserted between B and the drying vessel. Ozonised oxygen was then passed, and the tube allowed to cool. After the stream of ozone had been kept up for six hours, a mixture of carbonic oxide and highly ozonised oxygen, which had been prepared over sulphuric acid, was passed through the tube so as to displace the gases in it. The fine

openings at A and C were then closed with paraffin, and the tube allowed to stand for a week. The ozone used in the experiment was prepared by slowly passing oxygen backwards and forwards through a Siemens' induction tube five or six times between two glass gas holders over sulphuric acid; the carbonic oxide was then added.

On passing a spark through the mixture between wires which were 7 mm. apart, there was no explosion, but a considerable halo of blue light appeared round the path of the spark. From an analysis of the gases driven from the tube by a stream of carbonic acid the composition of the mixture was found to be

CO	36
Ozone.	8
Oxygen and air	56

The experiment showed that a considerable quantity of ozone did not confer inflammability on the mixture; the resistance to explosion could not in this case be due to the stability of the oxygen, for sufficient ozone was present to burn two-thirds of the carbonic oxide present.

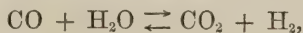
Lastly, I have to discuss a view as to the part played by moisture, which has not the advantage, enjoyed by the electrolytic theories, of embracing many phenomena apparently cognate. This supposes that in the collisions of carbonic oxide and oxygen molecules which occur when the mixture is strongly heated, the more violent collisions do not result in combination because the temperature of the product would be above its dissociation temperature. Steam, however, is not so easily dissociated as carbonic acid. When violent collisions occur between carbonic oxide and steam molecules, chemical change may result, since the heat of formation of carbonic acid from carbonic oxide and steam is small (9,200 cal.). The liberated hydrogen may recombine with oxygen since steam is stable under the conditions. An explosion, in short, is not propagated in the dry gases because the temperature of direct oxidation would be too high; in the presence of moisture, the explosion is propagated owing to indirect oxidation. The theory would *a fortiori* apply to the non-explosion of carbonic oxide and ozonised oxygen, for more heat is given out in the oxidation by ozone than by pure oxygen.

But it might be objected, since the quantity of steam necessary is very small, the amount of heat absorbed by it must be very small, and therefore the temperature reached by the carbonic acid would be practically the same whether it were formed directly in one stage (evolving 68,200 cal.), or in two stages (evolving 9,200 and 59,000 cal.). Although the total heat evolved would be the same in the two cases, the temperature of the interacting molecules might be very

different. In the direct oxidation of carbonic oxide, the heat of formation of 2 mols. of carbonic acid at constant volume would be sufficient to raise their temperature $8,030^{\circ}$, while in the indirect oxidation the same heat would be divided between 2 mols. of carbonic acid and 2 mols. of steam. Actually, if the oxidation is effected indirectly by a small quantity of steam, the steam molecules must react over and over again, and must rise in temperature; but the fewer the molecules of steam, the more slowly is the flame propagated, and meanwhile heat is lost by conduction to the walls. Again, it might be urged that dilution with an inert gas, such as nitrogen, should, on this hypothesis, cool the gas sufficiently to allow the formation of carbonic acid. But the molecular heat due to the direct union would for the moment be entirely in the carbonic acid formed, and would only be divided afterwards among the inert molecules.

Although the union of carbonic oxide and oxygen might thus be limited by dissociation, it is not necessary to suppose that in the burning of a damp mixture the oxidation of all the carbonic oxide must be effected by the steam. On the contrary, we can imagine that in the flame the slower collisions between carbonic oxide and oxygen result in the formation of carbonic acid.

With regard to the "inertness" of oxygen towards carbonic oxide in the incomplete combustion of hydrogen and carbonic oxide, I have stated that the phrase must be modified. In the equilibrium set up between the opposite chemical changes,



it was found that the ratio

$$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = \text{a constant},$$

provided that the oxygen taken was not more than enough to combine with the hydrogen in the mixture; with an excess of oxygen the ratio altered. I compared the effect of an excess of oxygen with that of an excess of nitrogen; both altered the ratio in the same sense. Accordingly I explained the alteration by the "inertness" of the oxygen towards the other three gases present, namely, CO, CO₂, and H₂O. I now see that the carbonic oxide and oxygen should be capable of combination behind the wave-front, and should not be called inert. But nevertheless the explanation may be in the main correct, for if carbonic oxide and oxygen could only combine together comparatively slowly, the excess of oxygen would retard the completion of the action, and thus have the same effect as an inert gas. According to the dissociation hypothesis, the hydrogen could combine with oxygen in the wave-front, and could reduce carbonic acid, but the carbonic oxide could not combine with the free oxygen until

the gases began to cool down. The period of combination would thus be prolonged just as the cyanogen flame is prolonged by inert nitrogen.

In the explosion of cyanogen with oxygen, the high temperature of the wave-front would prevent the direct union of the carbonic oxide formed there with the free oxygen; behind the wave-front, the carbonic oxide mixed with oxygen would fall in temperature below the dissociation point, and combination would begin. I think this hypothesis explains in a satisfactory way the lower intensity of the cyanogen flame when completely burnt, and the prolonged period during which the gases remain luminous behind the wave-front. I may add that both Bunsen and Deville held that the burning of carbonic oxide was retarded by dissociation.

It has been shown that carbonic acid is formed in the passage of the electric spark through the dried gases. The spark also causes dissociation in dried carbonic acid. It may be supposed in the latter case that the carbonic oxide and oxygen liberated by the heat of the spark partially combine on cooling, while the rest, rapidly mixed with inert gas by diffusion, escapes recombination. When the spark is passed in carbonic oxide and oxygen, the gases in its path, at first too hot to combine, are able to do so as they cool. In a mixture of the three gases, an equilibrium is reached when the rate of combination is equal to the rate of dissociation.

Again, the ready union of carbonic oxide and oxygen without flame on the surface of heated platinum may be explained on this hypothesis if we suppose that the platinum acts as a conductor to carry off the heat.*

But though the dissociation of carbonic acid explains some of the anomalies that have been discovered, there are still difficulties to be accounted for. In Smithells' experiment of the divided cyanogen flame, it is not easy to see why the carbonic oxide formed in the inner flame should burn in the outer when the flames are near together, but be extinguished on separating the two cones, unless we grant that freshly formed molecules have a power of combination which they lack when they have had time to "settle down." Possibly the heated gases formed by the first flame act like a metallic conductor, but in that case one would expect the flame of burning carbon bisulphide or cyanogen, when mixed with the carbonic oxide, would act in a similar way.

Brereton Baker (Trans., 1894, 617), who has carried out most patient and skilful experiments on the effect of moisture on chemical combination, is of opinion that there is a resistance to the direct union of elements (except in the nascent state), and that moisture

* An idea suggested by Professor Osborne Reynolds.

facilitates chemical union by allowing the transfer of the opposite electric charges of the molecules. In view of this opinion, and of the experiments lately made by J. J. Thomson, it appeared to me of interest to submit the dry mixture of carbonic oxide and oxygen to the Röntgen rays. Professor Schuster was kind enough to submit my tube to a very active discharge. The gases were contained in a thin soda-lime glass tube fitted with platinum wires. The Röntgen bulb was placed about 10 mm. from the eudiometer. Sparks having been passed through the dried gases without inflaming them, the Röntgen rays were turned on, and from time to time, during a quarter of an hour, a spark was passed through the gases, but no inflammation occurred. To prove the nature of the mixture, a small bubble of hydrogen (less than 0.4 per cent. of the total gas) was admitted to the dried gases. After a few minutes had been allowed for diffusion, a spark was passed, causing a violent explosion. The Röntgen rays, therefore, if they affect these gases at all, are not possessed of marked activity.

While I think the dissociation of carbonic acid at very high temperatures may be regarded as one of the limiting factors in the reaction between carbonic oxide and oxygen, it would seem that there is some other cause limiting the direct combination of these gases at lower temperatures.

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XLVII.—*On the Detonation of Chlorine Peroxide.*

By Professor H. B. DIXON, M.A., F.R.S., and J. A. HARKER, D.Sc.

M. BERTHELOT (*Sur la Force des Matières Explosives*, 1, 109) discovered the fact that certain endothermic gaseous compounds, *e.g.*, acetylene, cyanogen, and nitric oxide, could be decomposed by the detonation of a small charge of fulminate. The sudden shock arising from the fulminate is communicated, according to M. Berthelot, to the gas immediately round it, breaking down the chemical compound with liberation of heat; the heated molecules so produced in turn act on their neighbours, and thus the decomposition is propagated from layer to layer with the violence and the velocity characteristic of the explosion-wave.

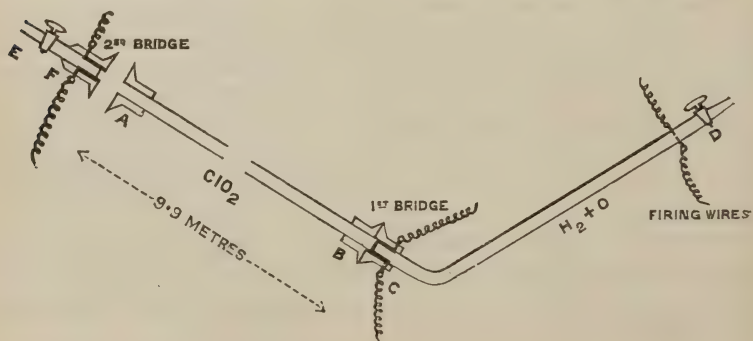
In 1889 Dr. Thorpe described to the Chemical Society the explosion of carbon bisulphide vapour, produced by means of a detonator. He adopted M. Berthelot's view, that the decomposition was of the nature of the explosion-wave.

According to this view, it would seem that the explosion, once initiated, should travel as far as the gas extends, and that the rate of the explosion should conform to the laws governing the propagation of the explosion-wave in gaseous mixtures. It appeared of interest, therefore, to determine whether the explosion, set up by the shock of the fulminate, was propagated along a tube filled with one of these endothermic gases; and, if so, to measure the rate at which the flame was propagated.

In 1891 we made experiments on acetylene and carbon bisulphide. In neither case could we succeed in setting up a true explosion-wave in a tube filled with these gases. Our explosion apparatus consisted of a steel bomb, holding 400 c.c., connected with a strong glass or a steel tube of 15 mm. internal diameter. A copper detonator holding 1 gram of fulminate was fired in the middle of the bomb. With acetylene, although the gas was completely decomposed in the bomb, the decomposition never extended more than 15 cm. down the tube. With the vapour of carbon bisulphide, on the other hand, the flame was more intense, and it travelled from 2 to $2\frac{1}{2}$ metres along the tube. The deposit of carbon and sulphur along the tube became gradually thinner until the explosion died out. A true explosion-wave was not set up (*Manchester Memoirs*, 1892). Last year M. Maquenne published in the *Comptes Rendus* some similar results with nitrous oxide and acetylene.

With chlorine peroxide, however, even when diluted with other gases, we have found that the explosion is propagated through a long tube.

The chlorine peroxide mixed with oxygen (and a trace of chlorine) was evolved by warming sulphuric acid and chlorate of potassium in a glass flask by means of a water bath; the gas was washed in a small bulb, and, passing through a sampling vessel, was conveyed by flexible glass tubing to the lower end of a long and stout glass tube, AB, 9.9 metres long, inclined at an angle of 30° . The two ends of



the long tube (made for us by Messrs. Molyneux and Webbe) were fitted with steel flanges, so that they could be readily clamped up to the two "bridge pieces." These bridge pieces, EF, CD, were steel tubes with taps at one end and flanges at the other. In both, an insulated bridge of silver foil was stretched across the tube close to the flange, by which an electric current was carried to the electromagnetic stylus on the chronograph. The silver bridge was coated, for protection, with paraffin. The lower bridge piece CD was bent; it was a metre in length, and was fitted with firing wires near the tap.

The chlorine peroxide passed into the tube without coming into contact with the metal flange, or any material other than glass. The explosion-tube was inclined, because it was found that the heavy peroxide flowed along the bottom of the tube without pushing the air before it when the tube was horizontal. When the long tube was filled, the flow of gas was diverted. The upper bridge piece was first clamped on, and then the lower; both being previously filled with electrolytic gas. On passing a spark through the electrolytic gas, the explosion-wave was set up, and this was communicated in turn to the chlorine peroxide in the glass tube. The flame was seen to suddenly illuminate the whole glass tube, the passage of the flame being too rapid to be followed by the eye.

We had many premature explosions of the gas, usually set up in the long tube. Only once did the explosion appear to start in the generating flask. At first, we attempted to prepare pure chlorine peroxide, but found it was impossible for us to fill the long tube and clamp on the bridge pieces without firing it; even with the diluted mixtures we used, we made seven experiments running, all of which failed at the last moment. The analysis of the sample showed considerable variations in the proportion of chlorine peroxide present, and we cannot be sure that the samples were of exactly the same composition as the gas in the tube.

Two experiments, we think, gave fairly trustworthy results:—

	Composition of mixture.	Rate of explosion, in metres per sec.
I. ClO_2	53.5	1065
O_2	46.5	
II. ClO_2	64.0	1126
O_2	36.0	

The rate of explosion of chlorine peroxide is thus of the same order as the rate of explosion in gaseous mixtures, in hydrogen and chlorine, for example. Unfortunately, the heat of formation of chlorine peroxide has not been determined, so that we cannot com-

pare the observed rate with the theoretical velocity calculated according to Berthelot's formula, or according to the "sound wave" hypothesis. Working backward from the latter, we should predict a heat of formation for ClO_2 of $-15,800$ cal. from the first experiment, and of $-16,800$ cal. from the second. It would be of interest to check this result by direct experiment.

From the density of the mixture and the velocity of the explosion, the pressure produced in the wave may be calculated by Riemann's equation.* According to this calculation, the faster explosion generated a pressure of 31 atmospheres in the wave.

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XLVIII.—*Morin*. Part I.

By HERMANN BABLICH, Ph.D., and A. G. PERKIN, F.R.S.E.

THE yellow colouring matter, morin, exists, as has been known for some time, in old fustic, the wood of *Morus* or *Maclura tinctoria*, and has lately been shown by one of us and F. Cope (Trans., 1895, 67, 937) to be also present in the Indian dyestuff "jackwood" (*Artocarpus integrifolia*). When pure it appears as a glistening mass of almost colourless needles, soluble in alkalis with a yellow coloration, and yielding, with aluminium mordants, very beautiful bright yellow shades.

Hlasiwetz and Pfaundler (*Annalen*, 1863, 127, 352) assigned to morin the formula $\text{C}_{12}\text{H}_8\text{O}_6 \cdot \text{H}_2\text{O}$, and described various crystalline monobasic salts to support this formula. Löwe (*Zeit. anal. Chem.*, 1875, 14, 119), however, considered the formula $\text{C}_{15}\text{H}_{10}\text{O}_7 + 2\text{H}_2\text{O}$ as more probable, and he obtained a lead salt, $2\text{PbO} \cdot \text{C}_{15}\text{H}_{10}\text{O}_7$; but although the percentage composition of the latter corresponded with this formula the molecular weight of morin was still open to doubt, it being considered by some as isomeric with maclurin, $\text{C}_{13}\text{H}_{10}\text{O}_6$, which, on analysis gives closely similar numbers. By means, however, of the compounds of morin with mineral acids, it was recently established by one of us and L. Pate (Trans., 1895, 67, 644) that its true formula is $\text{C}_{15}\text{H}_{10}\text{O}_7$, it being thus isomeric with quercetin. These acid compounds of morin are very similar to those of quercetin and fisetin, and differ from them only in the fact that during the formation of the sulphuric acid compound 1 mol. of water is eliminated.

By gentle reduction with sodium amalgam in acid solution, morin

* See Prof. Schuster's note, *Phil. Trans.*, 1893, 184, 152.

yields phloroglucinol and isomorin (Hlasiwetz and Pfaundler, *Jahresber.*, 1864, 537), a substance which in alkaline solution is readily reoxidised to morin; but when reduced in alkaline solution, it yields phloroglucinol and β -resorecylic acid (Hlasiwetz and Pfaundler, *loc. cit.*; Benedikt and Hazura, *Monatsh.*, 1895, 5, 167). By fusion with alkali, morin yielded resorcinol, phloroglucinol, and oxalic acid, and when oxidised with nitric acid β -resorecylic acid was the principal product. When distilled with sand (Benedikt, *Ber.*, 1875, 8, 606), morin yields, besides resorcinol, a substance paramorin, $C_{12}H_8O_5$, which crystallises from water in fine yellow needles.

Of the substitution products of morin, three only have been described, namely, morinsulphonic acid, $C_{15}H_9O_7 \cdot HSO_3$ (Benedikt, and Hazura, *loc. cit.*); tetrabromomorin, $C_{15}H_6Br_4O_7$; and tetrabromomorin ethyl ether, $C_{15}H_5Br_4O_7 \cdot C_2H_5 + 4H_2O$. The latter is formed by the bromination of morin in alcoholic solution, and can be converted into the free tetrabromo-derivative by digestion with zinc chloride solution and fuming hydrochloric acid (Hlasiwetz and Pfaundler, *loc. cit.*).

During the further study of the acid compounds of the natural yellow colouring matters, an account of which it is hoped shortly to lay before the Society, it was desirable to obtain some insight into the constitution of this colouring matter, and the following investigation was therefore instituted.

EXPERIMENTAL PART.

In the purification of the morin for this investigation, a method previously described was employed (Trans., 1895, 67, 650), namely, recrystallising it twice from alcohol and then converting the product into its hydrobromic acid compound to remove maclurin. After washing with acetic acid, the acid compound was decomposed by hot water in the presence of acetic acid, and the morin thus obtained in a pure condition.

Before proceeding with new work, it was thought advisable to restudy the decomposition of morin by fusion with alkalis, and its behaviour towards bromine.

Action of Fused Alkalis on Morin.

Morin was heated at 150–160° for half an hour with 10 times its weight of potassium hydroxide dissolved in a little water; the melt was dissolved in water, the solution neutralised with acid, extracted with ether, the extract evaporated, and the residue dissolved in a little caustic potash. After saturation with carbonic anhydride, the alkaline liquid was extracted with ether, the residue left on evaporat-

ing the ethereal extract being tested for phloroglucinol with the result that its presence was clearly proved.

To isolate the second product of the action, the remaining alkaline solution was neutralised with acid and extracted with ether; on evaporating the ethereal extract, a crystalline residue was obtained, which, after recrystallisation from water, formed colourless needles melting at 206° ; these, when dissolved in water, gave a red-violet coloration with ferric chloride. It had all the properties of β -resorcylic acid, and was found to be identical with it. As mentioned above, the products of this action previously obtained by others are phloroglucinol and resorcinol, the latter no doubt resulting from the decomposition of the resorcylic acid by the use of a higher temperature and longer heating.

Action of Bromine on Morin.

The study of this reaction was first carried out according to the directions of Benedikt and Hazura (*loc. cit.*).

To a solution of 5 grams of morin in 100 c.c. of alcohol, 9 grams of bromine were added, the mixture being then allowed to stand overnight. On the addition of water, the solution gradually deposited a dirty white precipitate, which was collected and purified by crystallisation from dilute alcohol. An ethoxy-determination of this substance by Zeisel's method gave the following result.

0.8772 gave 0.3260 AgI. $C_2H_5 = 4.56$.

$C_{15}H_5Br_4O_6 \cdot OC_2H_5$ requires $C_2H_5 = 4.48$ per cent.

In order to convert the tetrabromomorin ethyl ether into tetrabromomorin, the above authors recommend digesting it with zinc chloride and fuming hydrochloric acid. The hydriodic acid liquid from the above estimation was, however, found to contain tetrabromomorin in almost theoretical quantity, and this appeared to us to be a far preferable method for decomposing the ethyl ether.

The yield of tetrabromomorin by this alcohol process being but indifferent, experiments were carried out on the bromination of morin suspended in acetic acid, this method, as is well known, giving excellent results with quercetin and luteolin. After standing for 24 hours, the pasty mass thus produced was drained upon a porous tile, and purified by crystallisation from acetic acid. On analysis

0.1320 gave 0.1424 CO_2 and 0.0180 H_2O . $C = 29.40$; $H = 1.51$.

$C_{15}H_6Br_4O_7$ requires $C = 29.12$; $H = 0.97$ per cent.

The yield of tetrabromomorin obtained by this process averaged 80 per cent. by weight of the morin employed, being a far better result than that obtained by the alcohol method. If the product of the action of an acetic acid solution of bromine on morin be poured

into water, and the insoluble tetrabromomorin removed, the filtrate, on standing several days, gradually deposits a small quantity of a colourless, crystalline precipitate. This was collected and purified by several crystallisations from water. It then appeared as colourless needles, melting at 135° . This substance at first sight appeared to be tribromophloroglucinol, which melts at $149-151^{\circ}$ (Hazura, Benedikt, *Monatsh.*, 1885, **6**, 704), but numerous crystallisations did not raise the melting point given above, and, moreover, a bromine determination gave higher numbers (68.8 per cent.) than those required for tribromophloroglucinol (66.11 per cent.). It therefore suggested itself that here was probably a mixture of tribromoresorcinol and tribromophloroglucinol, both of which could well result from a decomposition of morin by means of bromine. As is well known, tribromophloroglucinol, when reduced in acid solution, is converted into phloroglucinol, and the latter can then readily be detected by means of the red coloration it gives with firwood and hydrochloric acid. The substance melting at 135° was examined in this way, and distinct evidence was thus obtained of the presence of *tribromophloroglucinol*.

When morin is digested with acetic anhydride and sodium acetate in the usual manner, or with acetyl chloride, for the purpose of obtaining an acetyl derivative, a colourless product is produced, which is difficult to crystallise, apparently on account of its very ready solubility in the usual solvents. After repeated purification, a small quantity was obtained in a crystalline condition, although still impure, but as, however, the tetrabromomorin yielded an acetyl compound more readily purifiable, the acetylation of morin itself was not further studied. The same was the case with the benzoyl derivative of morin, for although this is more readily crystallised than the acetyl derivative, yet, on account of its ready solubility, analysis showed that even after numerous crystallisations it was still contaminated with benzoic acid.

Pentacetyltetrabromomorin.—A mixture of one part of tetrabromomorin, one part of anhydrous sodium acetate, and three parts of acetic anhydride was boiled for one hour, the product poured into water, and after being allowed to remain for 24 hours, it was collected and purified by several crystallisations from alcohol.

0.1474 gave 0.2010 CO_2 and 0.0358 H_2O . $\text{C} = 37.1$; $\text{H} = 2.6$.

0.1158 „ 0.1038 AgBr . $\text{Br} = 38.1$.

0.3958 „ 0.3523 „ $\text{Br} = 37.92$.

$\text{C}_{15}\text{HO}_7(\text{Br}_4)(\text{C}_2\text{H}_3\text{O})_5$ requires $\text{C} = 36.9$; $\text{H} = 1.93$; $\text{Br} = 38.18$ p. c.

$\text{C}_{15}\text{H}_2\text{O}_7(\text{Br}_4)(\text{C}_2\text{H}_3\text{O})_4$ „ $\text{Br} = 40.71$ p. c.

It was obtained as colourless, prismatic needles, melting at 192—193°. On long boiling with alcohol, in which it is moderately soluble, it appears to undergo slight decomposition.

To determine the number of acetyl groups present in this compound, it was dissolved in a little boiling acetic acid, and the solution digested, after adding a few drops of sulphuric acid. On cooling, a semi-solid, crystalline mass of tetrabromomorin was obtained, which was treated with water, collected, washed, and dried at 160°.

0.5368 gave 0.4024 $C_{15}H_{10}O_7$. $C_{15}H_{10}O_7 = 74.94$.

$C_{15}HO_7(C_2H_5O)_5Br_4$ requires $C_{15}H_{10}O_7 = 74.63$.

It was therefore a pentacetyl derivative, and it is thus evident that there are *five hydroxyl groups* in morin itself.

Methylation of Morin.—To morin dissolved in a methylic alcohol solution containing five molecular proportions of caustic potash, excess of methylic iodide was added, and the whole digested at the boiling temperature for two days; to this solution five parts more of caustic potash dissolved in a little methylic alcohol was added, and the boiling continued for two days longer. After removing the methylic iodide and the greater portion of the alcohol by distillation, the residue was treated with water, extracted with ether, and the ethereal solution washed with dilute alkali and evaporated to dryness. The yellowish-brown oily mass thus obtained did not crystallise on standing; on dissolving it in boiling alcohol, however, and allowing the solution to stand for some hours, it deposited a crystalline product, which was collected and purified by several crystallisations from alcohol.

0.1404 gave 0.3260 CO_2 and 0.0646 H_2O . $C = 63.38$; $H = 5.11$.

0.1102 „ 0.2566 „ „ 0.0540 „ $C = 63.50$; $H = 5.44$.

0.1494 by Zeisel's method gave 0.3780 Agl. $CH_3 = 16.15$.

$C_{15}H_6O_3(OCH_3)_4$ requires $C = 63.68$; $H = 5.02$; $CH_3 = 16.76$.

The preliminary experiments on the methylation of morin were carried out with samples of morin which had been purified simply by recrystallisation from alcohol, with the result that the product obtained would not yield crystals when treated as above. Although morin when thus purified gives correct numbers on analysis, it still contains maclurin, for this has a similar percentage composition. It is indeed difficult to be certain when a sample of morin is chemically pure, unless it has been previously converted into the acid compound, and the treatment previously described in this paper has been resorted to. When purified by this means, no difficulty is experienced in obtaining from it a crystalline methyl ether.

Morin tetramethyl ether was obtained as a glistening mass of pale yellow needles, melting at 131—132°, moderately soluble in alcohol.

As has been shown above, morin contains five hydroxyls, and it is thus evident that one of these resists methylation. To be absolutely certain, however, of this, the behaviour of the methyl ether towards acetic anhydride was studied. One part of the ether, one of anhydrous sodium acetate, and excess of acetic anhydride were boiled for one hour, and the product then poured into water. After standing 12 hours, the colourless product was collected, drained upon a porous tile, and purified by crystallisation from alcohol.

0.1068 gave 0.2466 CO_2 and 0.0474 H_2O . $\text{C} = 62.97$; $\text{H} = 4.93$.

$\text{C}_{15}\text{H}_6\text{O}_3(\text{OCH}_3)_4(\text{C}_2\text{H}_3\text{O})$ requires $\text{C} = 63.00$; $\text{H} = 5.00$ per cent.

Monacetylmorin tetramethyl ether forms colourless needles, melting at 167° , sparingly soluble in alcohol. Morin therefore contains an hydroxyl group which resists methylation, and, as has been discussed in previous communications, this hydroxyl is evidently in the ortho-position relatively to a carbonyl group. To further support this fact, experiments were carried out to determine if morin tetramethyl ether would yield a potassium salt, this reaction having been shown by Kostanecki (*Monatsh.*, 1891, **12**, 318—322) to be a property of this class of substance. A saturated solution of morin tetramethyl ether in boiling alcohol, when treated with a few drops of alcoholic potash, deposited, on cooling, a mass of yellow needles of the potassium salt; these, when treated with water, were slowly decomposed, with regeneration of the free tetramethyl ether.

Decomposition of Morin Tetramethyl Ether with Alcoholic Potash.

Morin tetramethyl ether was heated with 10 parts of alcoholic potash in a sealed tube at 150 — 170° for two hours. The resulting light brown coloured liquid was extracted with ether to remove any trace of unchanged substance, and the aqueous solution saturated with carbonic anhydride. After extraction with ether (A), the liquid was neutralised with acid, again extracted with ether, and the latter ethereal extract (B) evaporated to dryness. The light brown, somewhat sticky residue, which did not crystallise on standing, was digested with a little boiling water, filtered, and the crystals which separated from the filtrate on cooling, were purified by recrystallisation from water. The product formed colourless needles, melting at 107 — 108° , and had the properties assigned to β -resorcylic acid dimethyl ether, with which it was evidently identical. The ethereal extract (A) on evaporation left a brown, sticky product, which gave the phloroglucinol reaction.

Morin Dimethyl Ether.—That portion of the product of the methylation of morin soluble in alkali, was dissolved in ether and the ethereal solution evaporated to a small bulk. A semi-crystalline deposit

separated on cooling, and from this the mother liquor was decanted and the residue dissolved in a little boiling alcohol. After standing for some hours, the crystals, which were then deposited, were collected, drained upon a porous tile, and crystallised first from alcohol, and finally from acetic acid.

0.0980 gave 0.2216 CO_2 and 0.0370 H_2O . $\text{C} = 61.64$; $\text{H} = 4.28$.

0.1424 „ by Zeisel's method 0.1955 Agl. $\text{CH}_3 = 8.76$.

$\text{C}_{15}\text{H}_8\text{O}_5(\text{OCH}_3)_2$ requires $\text{C} = 61.81$; $\text{H} = 4.24$; $\text{CH}_3 = 9.09$ p. c.

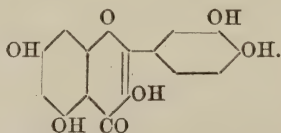
Morin dimethyl ether is obtained as a glistening mass of yellow needles melting at $225\text{--}227^\circ$, moderately soluble in alcohol.

Theoretical Considerations.

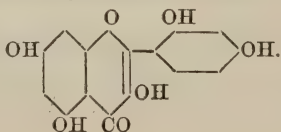
The results of this investigation show that morin, $\text{C}_{15}\text{H}_{10}\text{O}_7$, contains five hydroxyl groups, but that, as it yields only a tetramethyl ether, one of these hydroxyls is in the ortho-position relatively to a carbonyl group. The tetramethyl ether, on decomposition with alcoholic potash, yields resorcylic acid dimethyl ether, showing that in the original molecule the hydroxyl groups of the resorcinol nucleus are intact. Further, in respect to the fact that morin forms a tetrabromo-derivative, and that on fusion with potash it yields phloroglucinol and β -resorcylic acid, the work of others has been corroborated.

If the reactions of morin and quercetin be compared, a close similarity between these two yellow colouring matters is apparent, as they both combine with mineral acids, and contain five hydroxyl groups, one of which in each case is in the ortho-position relatively to a carbonyl group. Moreover, when fused with alkali, they yield respectively phloroglucinol and β -resorcylic acid, and phloroglucinol and protocatechuic acid and their tetramethyl ethers when decomposed with alcoholic potash give the dimethyl ethers of these acids.

Herzig has shown (*Ber.*, 1895, **28**, 293) that the formula of quercetin is

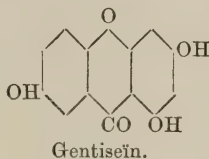
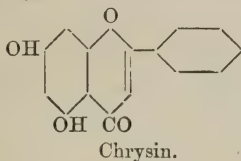


and the above results show that with little doubt the formula of morin may be represented as that of quercetin, in which the catechol nucleus has been displaced by resorcin, thus



As stated in the preceding paper, the fact that morin combines with mineral acids appears also to support this view.

The above formula for morin is interesting when considered in connection with its mordant dyeing properties, in that it does not contain two hydroxyl groups in the ortho-position relatively to one another, which is an essential characteristic of the dyes of the anthraquinone class. In this peculiarity, it may be classed with chrysin and gentisein,



both of which are yellow mordant dye-stuffs.

Quercetin in its catechol nucleus, contains two hydroxyls in the ortho-position relatively to one another but that to this is due its colouring property is doubtful, for morin dyes equally as well as quercetin.

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XLIX.—*Luteolin*. Part II.

By A. G. PERKIN, F.R.S.E.

IN a previous communication (this vol., 206), it was shown that the true formula of luteolin is $C_{15}H_{10}O_6$, a fact determined by the examination of its compounds with mineral acids and with bromine. The production of a tetracetyl and tetrabenzoyl compound also proved it to contain four hydroxyl groups, and a preliminary study of the behaviour of its alkali salt towards methylic iodide resulted in the production of a compound containing three methoxy-groups only. Since the publication of my results, Herzig (*Ber.*, 1896, **29**, 1013) has published a short paper in which he states that he is also working on luteolin, and at the same time mentions its acetyl derivative, methyl ether, and its behaviour towards fused alkalis. I must express my thanks to this gentleman for his courtesy in allowing me to see the manuscript of his paper before forwarding it for publication. As, through press of other work, I may be unable to complete my examination of this colouring matter for some little time, it appeared to me advisable to lay before the Society the net results that have been

obtained, especially as they have an important bearing on its constitution.

Ethylation of Luteolin.

One part of luteolin dissolved in a solution of 10 parts of caustic potash in ethylic alcohol, was boiled with excess of ethylic iodide and digested for 24 hours. After removal of the excess of ethylic iodide and the greater part of the alcohol by distillation, the residue was poured into water, the precipitated product dissolved in ether, and the ethereal solution, after being washed with dilute alkali, evaporated to a small bulk. The crystalline mass which separated on cooling was collected and crystallised repeatedly from alcohol until it had a constant melting point. On analysis,

0.1294 gave 0.3225 CO_2 and 0.0730 H_2O . $\text{C} = 67.97$; $\text{H} = 6.26$.

0.1555 „ (by Zeisel's method) 0.3000 AgI . $\text{C}_2\text{H}_5 = 23.79$.

$\text{C}_{15}\text{H}_7\text{O}_3(\text{OC}_2\text{H}_5)_3$ requires $\text{C} = 68.11$, $\text{H} = 5.95$, $\text{C}_2\text{H}_5 = 23.51$ p. c.

Luteolin triethyl ether is obtained as a glistening mass of light yellow needles melting at $131\text{--}132^\circ$, readily soluble in boiling, but almost insoluble in cold alcohol. It is insoluble in alkalis.

The residual hydriodic acid mother liquor from the Zeisel determinations was poured into water, treated with excess of sodium hydrogen sulphite solution, and the yellow flocculent precipitate which was produced was collected and crystallised from dilute alcohol. It formed a mass of light yellow needles, and was without doubt luteolin, for it yielded a colourless acetyl derivative melting at $213\text{--}215^\circ$. Herzig (*loc. cit.*) states that he has found the melting point of acetyl luteolin to be $225\text{--}227^\circ$. Feeling that it was possible some mistake might have occurred, I re-examined the melting point of my preparation, and, moreover, recrystallised it from alcohol with the result that the previous melting point, $213\text{--}215^\circ$, was not altered. By conducting the operation with rapidity, a slightly different result could be obtained, but in no case more than three degrees higher, and I therefore consider the melting point, $213\text{--}215^\circ$, to be correct. In experimenting with this tetracetyl-luteolin, I have observed that unless the product, which is of an exceedingly light and fluffy nature, is in good contact with the sides of the tube, erroneous results are liable to be obtained, and it is possible that this may account for the discrepancy above referred to.

It having been previously shown that luteolin contains four hydroxyl groups, whilst only a triethyl ether could be obtained, it appeared evident that the latter contains an hydroxyl group which resists ethylation; this being the case, it should yield an acetyl derivative.

To determine this point, one part of luteolin triethyl ether was

digested with one part of anhydrous sodium acetate and a slight excess of acetic anhydride for an hour; the solution was then poured into water and allowed to remain for 24 hours, when the colourless precipitate was collected, drained upon a porous tile, and purified by crystallisation from alcohol.

0.1196 gave 0.2934 CO_2 and 0.0654 H_2O . $\text{C} = 66.90$; $\text{H} = 6.07$.

$\text{C}_{15}\text{H}_6\text{O}_3(\text{C}_2\text{H}_3\text{O})(\text{OC}_2\text{H}_5)_3$ requires $\text{C} = 66.99$; $\text{H} = 5.82$ per cent.

Monacetyl-luteolin triethyl ether crystallises in colourless needles melting at $185\text{--}186^\circ$, sparingly soluble in alcohol.

It has been shown by Kostanecki (*Monatsh.*, 1891, **12**, 318—322), with the xanthenes and chrysin (*Ber.*, 1893, **26**, 2901), by Herzig with quercetin (*Monatsh.*, **5**, 72—93), by Schunck and Marchlewski with alizarin (*Trans.*, 1894, **65**, 185), and by myself with resorcylic acid (*Trans.*, 1895, **67**, 995), that it is not possible to ethylate by known methods the hydroxyl group occupying the ortho-position relatively to the carbonyl group in these substances. Kostanecki has, moreover, shown (*loc. cit.*), in the case of the ethers of gentisin and chrysin, that such compounds, when treated with alcoholic potash in alcoholic solution, yield intensely yellow, crystalline, potassium salts, which, however, on treatment with water, are decomposed, more or less readily, into potassium hydroxide and the free ether. Experiments with luteolin triethyl ether yielded a similar result, for, when a boiling alcoholic solution of this substance was treated with a few drops of alcoholic potash, glistening, yellow needles of the potassium salt were deposited, which, when treated with water, were at once decomposed yielding the free triethyl ether. It, therefore, appears that one of the hydroxyls in luteolin is in the ortho-position relatively to a carbonyl group.

Decomposition of Luteolin with Fused Alkalis.

It was previously shown (*loc. cit.*) that when luteolin is fused with potassium hydroxide, protocatechuic acid and a nearly colourless crystalline substance melting at 210° are the principal products. As this gives no coloration with chloride of iron, it was considered not to be phloroglucinol, although its melting point* indicated this substance. Herzig has stated (private communication and *loc. cit.*) that with small quantities of phloroglucinol the ferric chloride reaction was not trustworthy, a fact of which I was not aware, and that my substance was very probably phloroglucinol, as he had obtained evidence of its presence in the products of the action of fused alkali on luteolin by means of the fir wood and hydrochloric acid test. A small quantity

* The melting point of phloroglucinol varies according to the rapidity with which it is heated; on slowly heating (Baeyer, *Ber.*, 1886, **19**, 2186) it melts at $200\text{--}209^\circ$, and when quickly heated at $217\text{--}219^\circ$.

of luteolin was therefore again treated with fused alkali, and the products of the reaction separated as before; a solution of the substance melting at 210° gave the phloroglucinol reaction by the fir wood test. Luteolin, therefore, on fusion with alkali yields protocatechuic acid and phloroglucinol.

Decomposition of Luteolin Triethyl Ether with Alcoholic Potash.

Although only a small quantity of the triethyl ether was available it was of interest to determine whether it would yield protocatechuic acid diethyl ether on treatment with alcoholic potash, as the ethyl ethers of both quercetin and fisetin yield this compound under such circumstances.

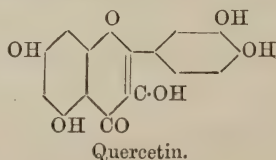
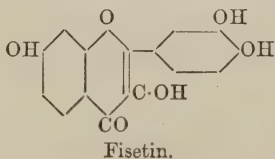
The triethyl ether was, therefore, heated with 10 parts of alcoholic potash in a sealed tube at $130-140^{\circ}$ for two hours, it having been previously found that it was but little attacked by digestion at 100° . The light brown liquid obtained was poured into water, extracted with ether which removed a trace of a light yellow substance, and the solution saturated with carbonic anhydride. After extraction with ether, the liquid was neutralised with acid, and the colourless precipitate collected and purified by crystallisation from alcohol. A mass of colourless needles was thus obtained which melted at $165-166^{\circ}$, and had all the properties of protocatechuic acid diethyl ether.

The ethereal extract of the liquid that had been treated with carbonic anhydride, on evaporation, yielded a light brown oily residue, which gave the phloroglucinol reaction. The quantity, however, was too small to admit of purification.

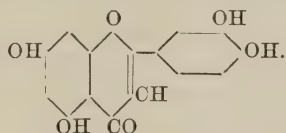
As previously stated, preliminary experiments on the methylation of luteolin resulted in the isolation of a methylic ether melting at $191-192^{\circ}$; this closely resembles the ethylic ether, in that it has now been found to have the formula $C_{15}H_7O_3(OCH_3)_3$, and to yield a monacetyl derivative, $C_{15}H_6O_3(OCH_3)_3 \cdot C_2H_3O$ (melting at $174-175^{\circ}$), and a yellow potassium salt. I hope shortly to be able to complete my examination of this substance.

Theoretical Considerations.

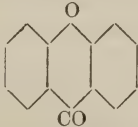
Fisetin and quercetin have been shown by Herzig (*Ber.*, 1895, **28**, 293) and Kostanecki (*ibid.*, 2302) to be derivatives of phenylated pheno- γ -pyrone, quercetin being a hydroxy-fisetin, thus



In the previous communication, a resemblance between luteolin and fisetin was pointed out in that they both had the same formula, contained four hydroxyl groups, and yielded dibromo-derivatives. Moreover, on fusion with potash, both give protocatechuic acid as one of their decomposition products, and they also combine with acids. On the other hand, as shown in this communication, in its alkyl derivatives luteolin more closely resembles quercetin, in that the latter, unlike fisetin, contains a hydroxyl in the ortho-position relatively to a carbonyl group. Quercetin also, on fusion with alkali, yields not only protocatechuic acid, but also phloroglucinol. It should also be remarked that when the ethylic ethers of luteolin and quercetin are digested with alcoholic potash, in each case the diethylic ether of protocatechuic acid is produced, showing that in the original molecule the hydroxyl groups of the catechol are intact, whereas one of those of the phloroglucinol nucleus is not. Most probably, therefore, the constitution of luteolin must be thus represented



this formula differing only from that of quercetin in that it contains no hydroxyl group in the pyrone ring. In other words, quercetin is also a hydroxy-luteolin. The acid compounds of luteolin appear to support this formula, for a further study of the behaviour of the natural yellow colouring matters towards acids, an account of which, I hope shortly to lay before the Society, has so far resulted in the fact

that no members of the xanthone, , or benzophenone

class, have been yet found which possess the property of combining with mineral acids, and it appears probable that this is a general reaction for the yellow colouring matters of the pheno- γ -pyrone class.

The absence in luteolin of a hydroxyl group in the pyrone ring may account for the greater permanency of its shades upon mordanted fabrics, as compared with those obtained with quercetin and fisetin.

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L.—*Constitution of the Cereal Celluloses.*

By C. F. CROSS, E. J. BEVAN, and CLAUDE SMITH.

THE general bearings of the subject of this communication have been dealt with in previous papers (Trans., 1894, **65**, 472; 1895, **67**, 433; *Ber.*, 1893, **26**, 2520; 1894, **27**, 1061; 1895, **28**, 1940 and 2604; *J. Amer. Chem. Soc.*, 1895, **17**; 1896, **18**, 8; *Chem. News*, 1896, **73**, 307). We have since followed up the special problem of the constitution of the cereal celluloses, more particularly with reference to the identity of their furfural yielding groups.

These celluloses we have assumed to be a complex of hexose groups on the one hand, and of groups allied to the pentoses on the other. That pentose molecules are not present as such is extremely improbable by reason (1) of the resistance of these celluloses to alkaline hydrolysis, (2) of their not giving the characteristic reaction with phloroglucinol and hydrochloric acid.

It is probable also, from the mode of formation of these celluloses in the plant, and the severe conditions of the alkaline hydrolysis by which they are isolated from the straws, that the complex is not a mixture of two celluloses, but a uniform aggregate of the two groups of molecules. The first object of the investigation was to determine the conditions of acid hydrolysis which would give a satisfactorily sharp separation of the constituent groups. The process ultimately adopted leaves nothing to be desired in this respect; the furfuroids are easily obtained in solution at the same time that the normal hexose groups are separated as a cellulose having the ordinary characteristics, and retaining only a fraction of the former group. Moreover, the furfuroids are obtained directly in a condition of molecular simplicity, which very much facilitates the work of determining the constants by which their identity is established. For the purposes of this preliminary discussion, we may anticipate the experimental proof of their identity. We shall be able to show that the members of this characteristic group of plant constituents are formal derivatives of a pentose, probably xylose.

A xylose monoformal, aggregated to its cellulosic form, is an addition to plant physiology, explaining many hitherto obscure points in the relationships of the furfural yielding carbohydrates.

It will be observed that a pentose monoformal, which we may represent as $C_5H_5O_3<\overset{O}{\underset{O}{\text{O}}}>CH_2$, has the empirical composition of normal cellulose, $C_6H_{10}O_5$. It appears also that the compound is formed in the plant from a hexose; and the process may be explained as the result of an oxidation of the terminal carbon atom, the

changes being formulated briefly as follows: . . . $\text{CH}\cdot\text{OH}\cdot\text{CH}_2\cdot\text{OH}$ becomes . . . $\text{CH}_2\cdot\text{OH}$ and $\text{H}\cdot\text{COH}$; formaldehyde is, however, not set free, but remains united by oxygen linking to the new pentose residue.

The oxidation is, therefore, one of internal rearrangement, that is without addition of oxygen from without. Transformations of this order are recognised as characteristic of the carbohydrates (Lobry de Bruyn, *Rec. Trav. Chim.*, 1894, **14**, 213), and it is unnecessary to enlarge on the probability of their occurrence in the plant. We have only to point out that the latter view of the origin of these compounds, is to be preferred, since all the evidence as yet available tends to negative the view that the pentoses are formed directly in the assimilating process (E. Fischer, *Ber.*, 1894, **27**, 3230; De Chalmot, *Ber.*, 1894, **27**, 2723), and further the association of the pentose and formyl residues in the original complex is quantitative, whereas on the former view there might very well occur a mixed complex of pentose or pentosan groups with the compounds in question.

Our present view, therefore, is that the terminal carbon atom of a hexose is first oxidised by internal rearrangement, and that the C-C union is then resolved, and oxygen linking substituted.

The question of the origin of the pentoses proper in the plant has been dealt with by De Chalmot in a series of publications (*Amer. Chem. J.*, 1894, **16**, 589; and also by Tollens, *Kohlenhydrate*, **2**, 60). De Chalmot regards the pentoses as formed by the destructive oxidation of the terminal $\text{CH}_2\cdot\text{OH}$ group of a hexose and elimination of the carbon as carbonic anhydride, but has been somewhat sceptical in regard to our contention that this oxidation may occur by stages, and that the intermediate terms are represented in plant tissues. Tollens has more recently dealt with the subject experimentally, and one of his recent communications (*Zeit. angew. Chem.*, 1896, **2**) contains the results of a preliminary investigation of possible solutions of this problem suggested by the introduction of a second CO group into the molecule of a hexose. By the action of potassium permanganate on starch, he obtained, in addition to formic acid in considerable quantity, an oxidised product which yielded furfural when boiled with dilute hydrochloric acid, and gave a characteristic purple reaction with phloroglucinol and hydrochloric acid. This colour reaction, which is quite distinct from that of the pentoses, is characteristic of the products of acid hydrolysis of the cereal celluloses, that is, of the formal-pentoses. There is ample ground for expecting the formation of similar products. With the more positive indications of identity, furnished by the results detailed in this paper, it will be easy to ascertain the presence, in complicated mixtures such as were obtained by Tollens, of intermediate terms of the

series, hexose : formal-pentose : pentose formate : pentose, so that a subject which for some time past has been dealt with by hypothesis framed from opposite but converging points of view, is now in the more satisfactory position of being attacked by definite experimental methods.

We proceed to a brief description of our experimental results, which supply a simple and clearly defined method of experimental enquiry.

The results group themselves under the following heads.

1. Investigations by methods of hydrolysis.

(a.) By treatment with sulphuric acid between the limits of concentration, $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$. This process was found difficult of control, and therefore abandoned.

(b.) By treatment at high temperatures with very dilute acids (1 per cent. H_2SO_4), the following conditions of treatment being finally adopted. 1 part of cellulose, and 6 parts of 1 per cent. H_2SO_4 ; rapid heating to 150°C . (3 atmos. pressure), and 15 minutes' heating at that maximum.

2. Proof of sharp separation of furfuroïds (solution) from the residue of normal cellulose (insoluble).

3. Proof of molecular simplicity of furfuroïds in solution.

(a.) Maximum numbers for cupric oxide reduction.

(b.) Maximum yields of osazones.

(c.) On fractionation, the melting points and composition of the osazones indicated the formation of osazones of pentoses.

4. Isolation of dissolved furfuroïds. Empirical composition, $\text{C}_6\text{H}_{10}\text{O}_5$, with high yields of furfural. Differentiation of reaction from those of pentoses.

5. Presence of formyl residue proved by oxidation with hydrogen peroxide, and quantitative estimation of the carbon dioxide formed, the results being confirmed by the synthesis, from pentoses and formic acid, of compounds which gave the characteristic reactions of the furfuroïds isolated from cereal celluloses.

In describing the experimental results, we shall find it convenient to use abbreviated expressions for "cupric reducing power" and for the yield of furfural when boiled under the standard conditions with hydrochloric acid (1.06 sp. gr.), namely, K for the percentage reduction referred to dextrose = 100; whilst F = percentage of furfural referred to 100 parts by weight of carbohydrate, or, in cases of solutions, calculated to 100 parts of dry solids (free from ash) in solution.

1. (a.) Process of solution in sulphuric acid.

The reactions of the normal celluloses with sulphuric acid are well

known. The concentrated acid behaves differently with the members of the two other sub-groups of fibrous celluloses (Trans., 1895, 67, 439), the reaction being complicated by condensations, with formation of dark-coloured products. These condensations, we may remark incidentally, are now accounted for by the presence of the formaldehyde residues in combination. In the hydrates of the series $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O} - \text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$, that is, of 1.65—1.55 sp. gr., on the other hand, the cereal celluloses dissolve to almost colourless solutions, and without constitutional change. We cite a typical experiment.

One gram of wheat-straw cellulose was dissolved in 6 grams of sulphuric acid of 1.65 sp. gr., and allowed to stand two hours in the cold, then diluted, and the reprecipitated cellulose collected, washed, dried, and weighed. The furfural was then estimated in both precipitate and filtrate. The results were as follows.

Straw Cellulose—F = 13.2, resolved into

Normal Cellulose insoluble.

Soluble products.

64.0 per cent. F = 0.9

36.0 per cent. F = 12.4

(The F, or furfural numbers, of the products are calculated to the original straw cellulose.)

It appears, therefore, that the furfuroïd constituents may be sharply separated by this process, and without constitutional change. On the other hand, this molecular condition in solution is still complex, as is indicated by the low cupric reduction, K being found = 13, which was raised to 28 only after two hours boiling of the highly diluted solution.

On neutralising with barium carbonate and filtering, a pale-coloured solution was obtained, which, on evaporation, left a nearly colourless, gummy residue, giving no pentose reaction (phloroglucinol), and containing traces only of barium compounds.

This method was then tried on a large scale, but the results were much less satisfactory. Preparations were obtained, as described, containing a large proportion of barium compounds, with low furfural numbers (F = 12—20), and low cupric reduction (K = 20—30).

These operations, on the scale of 1 kilo. of raw material, were kindly carried out for us by Mr. William Chattaway, of the Apothecaries' Hall. To him and the Corporation of the Apothecaries' Hall we are much indebted for this kind assistance.

The differential attack of the acid was therefore not maintained under the changed conditions of mass. Further careful investigation showed that small variations in the concentration of the acid, in the temperature and in the duration of digestion, produced large variations in the results. We cite one or two typical series in which the

effect of a particular factor was investigated by causing it to vary, the other factors remaining unchanged.

(1) Concentration of acid—

	Sp. gr.	Cellulose reprecipitated on dilution.	Constituents dissolved.
$\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}..$	1.55	71 per cent.	39 per cent.
$\text{H}_2\text{SO}_4, 2\frac{1}{2}\text{H}_2\text{O}.$	1.60	20 ,,	80 ,,
$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}..$	1.65	3 ,,	97 ,,

(2) Temperature—

	Cellulose reprecipitated on dilution.	Furfural numbers.	
		Precipitate.	Solution.
3°	96.0 per cent.	7.46	4.65
23	62.5 ,,	2.20	9.55

(3) Proportion of acid to cellulose—

	Cellulose reprecipitated.
3 : 1	23.0 per cent.
5 : 1	13.5 ,,
10 : 1	10.0 ,,

It needs no further evidence to show that the balance of conditions for the selective hydrolysis of the furfuroïds is difficult to control. The process was also unsatisfactory from the point of view of the condition of the furfuroïds in the dilute solution, the cupric reduction indicating that the CO-groups are largely unresolved. And again in the process of neutralising with barium carbonate there is a relatively large loss of the furfuroïds. This method of isolating the furfuroïds was therefore abandoned, partly on account of the difficulties thus experienced, chiefly, however, for the reason that experiments carried out simultaneously with the highly dilute acid (1 per cent. H_2SO_4) at elevated temperatures had given altogether satisfactory results.

(b.) The best conditions of digestion were determined by a series of comparative experiments with "brewers' grains," a closely allied substance, which has been investigated, especially with regard to the furfuroïd constituents, by Tollens. As the criterion of maximum effect, the cupric reducing power of the resulting solution was taken. The following table of results (next page) needs no further explanation than that the numbers in the last column represent the cupric reduction calculated in terms of dextrose and of the original weight of "grains."

With this material, as with the cereal celluloses, it was found that the furfuroïd constituents are satisfactorily exhausted and converted into soluble derivatives.

We shall refer subsequently to the composition of the products obtained in the above experiments, but for the present we confine

ourselves to drawing the one obvious conclusion from the numbers, namely, that for the maximum effect the essential conditions of the treatment are (1) a highly dilute acid (1 per cent. H_2SO_4 has been adopted); (2) a temperature of $133\text{--}143^\circ$, corresponding with 3—4 atmos. steam pressure; the lower limit has been adopted.

Invariable Conditions.

Weight of "Grains" 80 Grams.

Volume of Solution, 500 c.c.

Experiments on varying Conditions.

Pressure.	Time.	Strength of acid.	Yield of reducing sugar.
No. 1, 9 atmos.	15 mins.	0.5 per cent.	17.19 per cent.
" 2, 9 "	15 "	1.0 "	17.39 "
" 3, 8 "	15 "	0.5 "	19.24 "
" 4, 8 "	15 "	1.0 "	19.49 "
" 5, 7 "	15 "	1.0 "	22.48 "
" 6, 7 "	15 "	0.5 "	20.58 "
" 7, 7 "	15 "	0.75 "	22.85 "
" 8, 7 "	15 "	1.5 "	22.48 "
" 9, 6 "	15 "	0.75 "	26.11 "
" 10, 6 "	15 "	1.0 "	27.6 "
" 11, 5 "	15 "	1.0 "	28.65 "
" 12, 4 "	15 "	1.0 "	35.67 "
" 13, 3 "	15 "	1.0 "	37.96 "
" 14, 2 "	15 "	1.0 "	30.48 "
" 15, 1 "	15 "	1.0 "	very slight
" 16, 3 "	15 "	1.5 "	37.96 "
" 17, 3 "	10 "	1.0 "	35.67 "
" 18, 3 "	30 "	1.0 "	37.0 "

The following further details and results of a typical experiment with a straw cellulose may be cited. 80 grams of the cellulose digested with 500 c.c. of 1 per cent. H_2SO_4 under the conditions described, gave the following.

The Products of Hydrolysis.

(a.) *Insoluble.*—The residual cellulose, which was only faintly coloured, weighed 55.5 grams, that is, 69 per cent. of the original.

On combustion it gave $\text{C} = 45.2$; $\text{H} = 5.6$ per cent.

On boiling with hydrochloric acid of 1.06 sp. gr., it yielded 2.3 per cent. of furfural, equal to 1.6 per cent. on the original cellulose.

On conversion into thiocarbonate, it gave a solution of normal characteristics, yielding tenacious films when evaporated upon a glass surface.

Comparing this residue with the one obtained by reprecipitation from solution in $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ in a successful experiment, we note the following differences. The latter, on combustion, gave the mean numbers $\text{C} = 43.0$; $\text{H} = 6.5$ per cent., and a furfural number $\text{F} = 1.6$.

The difference is merely a difference of hydration due to the corresponding difference in the conditions of treatment.

(b.) *Soluble*.—The solution was pale yellow, and smelt of furfural. The quantity of free furfural was, however, small, representing 0.1 per cent. of the total dissolved constituents. The total quantity of organic solids in solution represented 28 per cent. of the original solids. The furfural number was found to be $\text{F} = 39.5$. Taking, therefore, the furfural numbers of soluble residue and dissolved products, and calculating to the original cellulose, we obtain

$$\begin{array}{r} 70 \times 2.3 = 1.61 \\ 28 \times 39.5 = 11.06 \\ \hline 12.67 \end{array}$$

which satisfactorily accounts for the total furfuroïds of the original cellulose, for which $\text{F} = 12.8$.

The process, therefore, gives a satisfactorily sharp separation of the furfuroïds from the remaining groups which constitute a normal cellulose, and there is satisfactory evidence of the absence of constitutional change; it appears to be a process of simple hydrolysis.

3. That the soluble carbohydrates are in a condition of molecular simplicity, that is, fully hydrolysed, is proved.

(a.) By the cupric reducing power of the solution. A large number of such determinations have been made in the course of these investigations, both by volumetric and by gravimetric methods; the numbers show the unusual maximum, $\text{K} = 130$, with a range of variation between 110 and 130. These numbers further indicate the presence of a molecule or residue of pentose constitution, the C_5 aldoses having a cupric reducing power of $\text{K} = 105$ —115. Comparative observations were made with pure xylose and arabinose in solutions of the same concentration as the solutions of the furfuroïds in question, and under similar conditions. The numbers obtained were $\text{K} = 105$ —112.

(b.) The yields of osazones were also exceptionally high. Several determinations were made from time to time with different solutions, averaging 3 per cent. of total dissolved solids. The average yield of osazone was 30—40 per cent. of the weight of carbohydrate in solution.

Maquenne has determined the yields of osazones from typical

carbohydrates in dilute solution (1 : 100), and obtained the following numbers (*Compt. rend.*, 1891, **112**, 799).

Fructose, 70 per cent.; xylose, 40 per cent.; arabinose, 27 per cent.; dextrose, 32 per cent.

As our osazones were formed in 3 per cent. solutions, we made observations with xylose and arabinose in solutions of this concentration and under conditions identical with those which obtained with the carbohydrate under investigation; the yields of osazones were from xylose 25 and from arabinose 16 per cent. It is sufficiently evident, therefore, that in the soluble products of hydrolysis of the cereal cellulose we are dealing with a carbohydrate in its fully hydrolysed form.

We have now to record the experimental evidence for the actual identity of the compound.

The results already noted indicate a close relationship to the pentoses. The fractionation of the osazones revealed the presence of small quantities of osazones of low melting point ($135\text{--}143^\circ$), but the main mass was obtained in fractions melting between the limits 146° and 153° . Not only in melting points, but in all respects the osazones were indistinguishable from those of the typical pentoses, xylose, and arabinose.

The results of ultimate analysis were also in close accordance with the requirements of a pentosazone formula. The following are the numbers obtained.

	(1).	(2).	Calculated for Pentosazone, $\text{C}_5\text{H}_8\text{O}_3(\text{N}_2\text{HPh})_2$.
N	17.1	17.3	17.07 per cent.
C	62.5	62.3	62.2 ,,
H	6.4	6.5	6.1 ,,

As the osazone obtained from the soluble products of hydrolysis of straw cellulose was indistinguishable from xylosazone, it would appear that the carbohydrate in question is either xylose or a closely related compound.

4. The solution, on the other hand, did not give the reaction of the pentoses with phloroglucinol, but an equally characteristic reaction, namely, the development of a deep violet coloration with separation of an insoluble, blue-black compound.

We proceeded with the investigation of this divergence by attempting to isolate the compound by evaporation and crystallisation; for this purpose, the solution was first neutralised with barium carbonate and filtered. Traces only of barium compounds were present in the filtered solution, which was evaporated to a syrup, and kept for some weeks in a desiccator, but there were no signs of crystallisation. The compound was, therefore, dried at $100\text{--}105^\circ$; the residue was

an amorphous, gummy substance, brittle when dry, and almost colourless.

On combustion, we obtained the following numbers.

	I.	II.	Calculated for $C_6H_{10}O_5$.
C	44.2	44.5	44.44 per cent.
H	6.7	6.3	6.17 „

These numbers and the yields of furfural (38—42 per cent.) confirm the observation of divergence from the composition and properties of the pentoses and pentosans. We appear, therefore, to be dealing with a derivative of a pentose.

5. The effect produced on the compound by numerous processes of oxidation were studied; certain oxidising agents, when added gradually to the warm solution, determine the formation of formaldehyde, easily recognised by its odour and the reactions of the solutions obtained on distilling. The most characteristic oxidation, however, is that produced by hydrogen peroxide; on adding this reagent (20 vol. solution) in quantity corresponding with 1 atom of oxidising oxygen to 1 mol. of $C_6H_{10}O_5$, and warming, formaldehyde is liberated; effervescence then commences, and at the same time an amorphous compound is precipitated, but, on continuing to heat, this compound is dissolved again, with increased effervescence.

That the effervescence is due to the liberation of carbonic anhydride was proved by quantitative observations, the evolved gases being first passed through a drying tube containing calcium chloride, and then absorbed by potassium hydroxide. The results were satisfactorily constant, the following numbers being obtained in experiments in which the peroxide was added in excess (3—5 atoms of oxygen as H_2O_2 per molecule of $C_6H_{10}O_5$).

	I.	II.	III.
CO_2 estimated	19.5	20.5	20.1 per cent.

On this evidence we concluded that the compound $C_6H_{10}O_5$ is a compound of pentose and formic residues, the second CO-group being united by an oxygen linking to the pentose residue.

From a compound represented by the formula $C_5H_8O_3 < \overset{O}{\underset{O}{\text{C}}} > CH_2$, we may calculate the yields of the products of decomposition.

(1) CO_2 by oxidation of the formal group.

(2) Furfural by the ordinary process of condensation of the pentose, first liberated by hydrolysis as follows.

(1) $C_6H_{10}O_5$ yields $CO_2 = 27.1$ per cent.

(2) $C_6H_{10}O_5$ yields $C_5H_{10}O_5$ which yields 48 per cent. of furfural.

And this calculated to the original $C_6H_{10}O_5$ is $150 \div 162 \times 48 = 44.0$ per cent. Taking into account that we have been unable to

crystallise the product or otherwise to separate it in a condition of purity, and that these decompositions are not strictly quantitative, there is sufficient concordance between the experimental and calculated numbers to bear out our conclusion as to the identity of the compound.

The synthesis of compounds of formaldehyde with the carbohydrates does not appear to have been attempted. The aldehyde readily reacts with the corresponding alcohols, mannitol, for example, with formation of crystalline compounds, formals of considerable stability and resistance to acid hydrolysis (Schulz and Tollens, *Annalen*, 1895, 289, 20). The reaction requires the presence of powerful condensing agents, and it may be, therefore, difficult to devise suitable conditions for the simple combination of formaldehyde with the alcoholic OH-groups of the pentoses. The subject is an attractive one, and we hope before long to be in possession of more direct verification of the results of this investigation, by comparing the "natural" with the laboratory products.

Formic acid, on the other hand, appears to react readily with the pentoses under conditions of condensation involving no fundamental change of the carbohydrate. On warming the pentoses, in solution, with formic acid in presence of hydrochloric acid, compounds are obtained giving the purple reaction with phloroglucinol, identical with that of the compounds under investigation. It is not probable, however, that the latter are formates or formic acid ethereal salts derived from the pentoses. In the first place, they could hardly survive the severe alkaline treatment by which the cereal celluloses are isolated from the straws; secondly, no acid groups are present among the products of hydrolysis whether this is effected by the concentrated or dilute acid; thirdly, the ultimate analysis of the products establishes a carbohydrate formula.

It is not improbable, however, that a formal derivative and a formate should give an identical colour reaction with phloroglucinol when warmed with hydrochloric acid of 1.06 sp. gr.

In the above account of experimental results, we have kept strictly to the positive evidence of identity of the particular furfuroïd under investigation. We regard this as established in general terms.

Certain minor issues of the work we have postponed until the main argument was complete. They may be dealt with *seriatim*.

1. The presence of one or more products of hydrolysis in the solutions obtained by the action of acids on the cereal celluloses.

We have assumed that the dissolved solids represent one compound only, namely, the formal-pentose.

The absence of hexose compounds has been established by investigation of the products formed on oxidation by nitric acid; neither

saccharic nor mucic acid is formed, but the proportion of oxalic acid is high, and nitroso-compounds are also formed in large proportion. A series of compounds of acidic nature, giving calcium salts insoluble in acetic acid were also obtained; these all contained nitroso-groups, and burned more or less explosively on heating to 200—300°. To obtain these compounds in quantity sufficient for complete investigation, we intend to operate on a large weight of the original substance.

The absence of hexose groups is in accordance with what we know of the degree of resistance of the normal celluloses to acid hydrolysis. Cotton cellulose, when treated under the conditions adopted for resolving the cereal celluloses, lost in weight 5·7 per cent., and the products in solution showed the maximum reduction of CuO, that is, were present as dextrose.

We regarded it as probable, therefore, that the hydrolysed furfuroïds would be accompanied in solution by a certain proportion of hexose compounds; but that the latter are actually present in only fractional proportion is shown (1) by the results of nitric acid oxidation, (2) by the non-formation of osazones of high melting points, (3) by the high furfural numbers of the solution calculated to the total dissolved solids.

2. *The Oxidation by Hydrogen Peroxide.*—It may be objected that there is not sufficient evidence for the conclusion that the evolution of carbonic anhydride is due to the decomposition of a formyl residue. It has been stated by C. Wurster that the carbohydrates themselves are oxidised by the peroxide with liberation of carbonic anhydride (*Centralbl. f. Physiol.*, 1, 33), though the action is very slow; we have, therefore, kept this possibility carefully in view.

The following experiments on xylose and arabinose, under conditions of treatment identical with those employed in investigating the furfuroïds are of interest. No carbonic anhydride was evolved, but that a certain amount of oxidation had taken place was shown by the change in the fufural number.

No. of atoms O, as H_2O_2 per 1

mol. pentose	0.	1.	2.	3.
Furfural obtained from product—				
Arabinose.....	49·0	35·6	34·4	34·4
Xylose.....	51·0	48·5	—	42·2

The action on xylose is therefore slight; on arabinose more pronounced, but reaches a limit, whilst the furfuroïd under investigation shows a behaviour differing from that of the pentoses of known constitution. Treated under the conditions mentioned above, and examined for furfural after oxidation, the following numbers were obtained.

	Original.	After oxidation (hydrogen peroxide) with		
		1 at., O.	2 at., O.	3 at., O.
Furfural	42.0	29.3	11.4	5.3

This more pronounced oxidation of the pentose residue is accounted for by the fact that it is a residue, and consequently the entrance of the oxidising groups is facilitated where the formaldehyde residue is split off; the divergence does not necessarily imply a constitution or configuration different from that of the known pentoses. The constants of the osazone, and the specific rotation of the original furfuroïd ($[\alpha]_D = 26^\circ$) are almost identical with those of xylose. The evidence, therefore, is sufficiently strong to justify the conclusion that it is in effect a xylose-formal.

De Chalmont, in a paper on the formation of pentoses in the plant (*Ber.*, 1894, 27, 2723), points out, on the one hand, the similarity in configuration of *d*-glucose with *l*-xylose, and of *d*-galactose with *l*-arabinose: and, on the other, that these carbohydrates occur in plants and plant products in corresponding pairs. We have, therefore, this *a priori* presumption in favour of the xylose residue in the cereal straws.

3. *Action of Bromine.*—Bromine is rapidly absorbed by the acid solution of the furfuroïd, and if the bromine be added until a slight excess is present the quantity taken up will be from 21 to 25 per cent. of the weight of the furfuroïd; the bromine is found to be exclusively in the form of the hydracid. On adding bromine in like manner to the neutralised solution, removing the slight excess, and titrating the free acid present, the latter was found to correspond exactly with the amount of hydrogen bromide calculated from the weight of silver bromide directly precipitated. The action of the bromine is therefore one of oxidation, and no unsaturated groups are present. The bromine calculated to an equivalent of oxygen ($\text{Br}_2 = \text{O}$) works out to only a fractional molecular proportion of the furfuroïd; the action, therefore, is at first selective, the formaldehyde being oxidised to carbonic acid. The yield of osazone is considerably increased, but is identical in composition and properties with that obtained from the original solution. These results generally confirm the conclusions as to the identity of the furfuroïd.

4. Other comparisons were instituted with pentoses of known constitution, such as oxidations by permanganate and by chromic acid: the results were confirmatory. The action of dilute alkalis on this group of aldoses is also noteworthy. On adding sodium hydroxide in excess (0.5 per cent. NaOH on the solution), and warming to 70–80° the furfuroïd is rapidly changed; the cupric reducing power falls

in a few minutes to one-fifteenth of the original, and a new complex of products is present, a characteristic feature of which is the large yield of iodoform obtained on warming the alkaline solution with iodine. The pentoses were also found to be very sensitive to the action of alkalis; this point is noteworthy from the fact that the cereal celluloses are themselves resistant to the action of alkalis, so far as regards the "furfuroïd" configuration.

5. *Fermentation (Yeast).*—The solutions obtained from the cereal celluloses by the action of acids, when neutralised, ferment rapidly with fresh, washed yeast. A limit is, however, soon reached, and on investigating the unfermented residue it is found that the cupric reduction has fallen to 60—70 per cent. of the original, and the furfural number to 70—80 per cent. of the original; a partial fermentation of the furfuroïds therefore occurs, with formation of alcohol and carbonic anhydride. We shall revert to this point in dealing with the question of the composition of the original straw. These observations further confirm the evidence furnished by the more important constants of the compounds in question.

We have only now to point out the physiological significance of this diagnosis of the constitution of the cereal celluloses. The evidence as to assimilation leads to the conclusion that the higher plants build up, in the first instance, *d*-glucose and *d*-fructose and their polysaccharides, if not exclusively, at least in overwhelming proportion (E. Fischer, *Ber.*, 1894, **27**, 3230). Assimilation is followed by the indefinitely wide range of secondary changes which accompany and determine the play of individual and group characteristics of structure and composition.

Next, in order of chemical significance, to hexose-formation is the appearance of a second CO-group in the C₆-molecule. We have endeavoured, in the investigation cited above, to trace this molecular change, the occurrence of which is very clearly indicated in the constitution of the lignocelluloses. We followed, in the first instance, the hypothesis of a process of direct or extrinsic oxidation. The results of a two years' study of tissue formation in the barley plant tended to negative this hypothesis (*Ber.*, 1895, **28**, 2604). The results of the study of the cellulose basis of the cereals now indicate that the origin of a second carbonyl may take place by a process of intrinsic change, that is, the migration of an oxygen atom within the hexose molecule. To this view we ask the careful attention of physiologists. It is consistent with all that is known of the chemistry of the carbohydrates considered as isolated compounds, and as they have an obviously increased mobility within the arena of cell vitality, the occurrence of such a process might well have been predicted. It is more satisfactory, however, to have arrived at the conclusion by way of

positive evidence, for that furnished by our investigations is certainly definite, if not finally conclusive, in respect of the actual constitution and configuration of the typical product. These points are under further investigation. Chemists will readily appreciate the increased range of possible transformations, provided for by the duplication of the CO-group of an aldose. Without, however, speculating on probabilities, these considerations find an immediate application to the chemistry of lignification. The characteristic groups of the lignocelluloses are undoubtedly of quinonic type; and they are also invariably associated with furfural-yielding groups. The ultimate purpose of these investigations is to trace the probable genetic relationships of these typical groups; and we have, therefore, extended to the province of the lignocelluloses the methods and conclusions dealt with in this communication. The results of this further investigation will form the subject of a separate paper, and we, therefore, merely outline, in conclusion, some of the more important results arrived at.

(a.) The lignocelluloses of the cereals, for example, the straw and seed envelopes (as obtained in brewers' grains) are similarly attacked by acid reagents, their furfuroïd constituents being hydrolysed to soluble forms and separated from the complex of cellulose and unsaturated (keto-hexene) molecules.

(b.) These furfuroïds have characteristics similar to those isolated from the celluloses: but the hydrolysis of the parent molecule proceeds to a lower limit; the cupric reduction of the soluble furfuroïds is relatively low, and the osazones are of lower melting point ($120-130^{\circ}$).

(c.) In regard to alcoholic fermentation, however, the furfuroïds are obtained in a more sensitive condition. Thus, in the case of barley-straw treated with $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$, the solution, after dilution and filtration from the reprecipitated ligno-cellulose complex, was examined for the above constants, then neutralised and fermented, and the constants of the unfermented residue determined. The following are the results.

	K.	F.
Before fermentation	43.5	32.3
After fermentation	2.3	8.1

The soluble furfuroïds were therefore, to a very great extent, fermented. It appears, also, from the researches of W. E. Stone, published in the *American Journal Agricultural Science*, 1893, 7, 6, that of the total furfuroïds in a typical selection of fodder plants, a large proportion, 60—80 per cent., are digested on passing through the alimentary tract of herbivora.

On the other hand, it is positively established that the pentoses

proper are not susceptible of alcoholic fermentation, neither are they assimilated in the process of animal digestion.

The results, therefore, further indicate that in the cereal stems the furfuroïd constituents are not pentosans, but products representing stages intermediate between the hexoses and pentoses.

We gratefully acknowledge at this opportunity the assistance we have received in carrying out these researches. A substantial grant from the British Association, through the kind offices of Mr. R. Warington, F.R.S.; a grant from the Chemical Society Research Fund. To Messrs. Augustus Voelcker & Sons we are indebted for ample laboratory accommodation; and to our assistant, Mr. O. W. Dahl, for valuable incidental help.

LI.—*Ethereal Salts of Optically Active Malic and Lactic acids.*

By THOMAS PURDIE, F.R.S., and SIDNEY WILLIAMSON, Ph.D.

THE tendency of optically active compounds to become racemised when undergoing chemical change presents a serious obstacle to the preparation of their derivatives, and the difficulty is much enhanced by the fact that, except in a few instances, the exact conditions under which racemisation occurs are imperfectly known. It is generally recognised that in dealing with such substances high temperatures and violent actions are to be avoided; but, even when every precaution has been taken, and an active derivative obtained, there is always a risk of its activity having been impaired by the production of more or less of the racemoid form, the presence of which cannot in most cases be directly detected. In preparing such derivatives with the view of determining their constants of activity, it is therefore essential either to recover the compounds from which the derivatives under investigation were obtained, so as to compare their activities with those of the original substances used, or, if this is impossible, to employ various methods of preparation, and to show that the activity of the different specimens is identical.

In recent times, numerous series of optically active ethereal salts have been prepared in connection with the interesting questions raised by Guye's theory. In some instances, as, for example, that of the active glycerates prepared by Frankland, of the amylic ethereal salts prepared by Guye and Chavanne (*Compt. rend.*, 1894, **119**, 906), and by Walden (*Zeit. physikal. Chem.*, 1894, **15**, 645), precautions of the kind referred to, have been adopted, but in numerous other cases no evidence of the absence of the racemoid compound appears to have

been sought, and, as the problems under investigation are chiefly of a quantitative kind, it is obviously quite uncertain what value, if any, is to be attached to the optical data thus obtained.

That precautions such as those mentioned are indispensable, if the data sought for are to have any quantitative significance, is abundantly evident from the results obtained by J. Wallace Walker in the preparation of the ethereal salts of active lactic and halogen propionic acids (*Trans.*, 1895, **67**, 914). He finds, for example, that the specific rotation of methylic lactate, procured from the silver salt, is far in excess of the values previously quoted by others for the same substance prepared by the direct action of the acid on alcohol. He also finds that the bromopropionates prepared by the action of phosphorous pentabromide on the ethereal lactates, are much more active than those obtained by the direct action of that reagent on lactic acid and subsequent treatment of the acid bromide with alcohol, the amount of inactive compound produced by the latter method amounted in one case to 50 per cent. of the whole, in spite of every precaution being taken to keep the temperature as low as possible. The specific rotations previously quoted by Walden (*Ber.*, 1895, **28**, 1293) for the chloro- and bromo-propionates are thus entirely erroneous, Walker's results being in every case far in excess of them. As the difference amounted in some cases to 50 per cent., Walker attributes the low activity of Walden's ethers in the main to partial racemisation occurring in the course of their preparation, and not to the impurity of the original lactic acid used, although the low activity may have been partly due to the presence of foreign substances of opposite activity. In further illustration of the serious errors that may arise in the preparation of the derivatives of active acids, it may be mentioned that the specific rotation found by Walden for ethylic ethoxysuccinate (*Zeit. physikal. Chem.*, 1895, **17**, 252) is 1.44° , whilst the value found by us was over 55° (*Trans.*, 1895, **67**, 972). It is, moreover, particularly essential that the rotations of such simple substances as the ethereal salts of malic and lactic acids should be correct, as they often form the starting points for the preparation of a large number of more active derivatives, in which, of course, any initial error is largely increased.

We may take the opportunity here of recording a remarkable instance of total racemisation which we recently observed in the course of an attempt to prepare the active alkylic hydroxypropionates, although the conditions observed were such as, it might have been supposed, would preclude the occurrence of any such change. The method used was that described by Schreiner (*Annalen*, 1879, **197**, 12) for the preparation of the corresponding inactive compounds, namely, the action of sodium alkylate at the ordinary temperature on

ethereal α -halogen propionates; 11 grams of dextro-ethylic α -chloropropionate, showing a rotation of $+18.75^\circ$ in a 100-mm. tube, were added very slowly to a cold alcoholic solution of sodium ethoxide containing one atomic proportion of sodium. The liquid became quickly turbid from separation of sodium chloride; after some time, it was gently heated, then treated with carbon dioxide to decompose any possible small excess of sodium ethoxide, filtered, and distilled under reduced pressure. The distillate was quite inactive. The analysis of the silver salt obtained from the neutralised product of hydrolysis showed that ethylic ethoxypropionate had been formed; the salt was found to contain 48.03 per cent. of silver, the calculated percentage for $C_5H_9O_3Ag$ being 48.00.

As it seemed possible that racemisation might have been caused by the presence of excess of sodium ethoxide during the action or by the subsequent distillation of the product, a second experiment was made with lævo-ethylic bromopropionate in which these sources of error were avoided. The calculated quantity of alcoholic sodium ethoxide was added, a small portion at a time, to the ethereal salt; the mixture was kept cool with ice, and allowed to become neutral after each addition of the alkylate before a fresh quantity was added. The action under these conditions proceeded very slowly, and took two days for its completion. The alcoholic liquid was then filtered from precipitated sodium bromide, and examined without previous distillation. It was quite inactive. It is difficult to see why the change of configuration implied in racemisation should have been directly induced under the conditions described. The result certainly suggests the question whether, in general, chemical changes in which halogen atoms are replaced by oxyalkyl groups by the action of sodium alkylate are simple cases of substitution, or whether the action really consists in the splitting off of halogen acid and the subsequent addition of a molecule of alcohol. The latter explanation seems probable, as it has previously been shown that various unsaturated ethereal salts, the acrylates among the number (Trans., 1891, 59, 474), possess the property of combining with alcohol in the presence of small quantities of sodium alkylate.

In the preparation of the numerous series of optically active ethereal salts, which have been recently investigated in connection with Guye's theory, the method of etherification by means of hydrochloric or sulphuric acid has usually been employed. That mineral acids at high temperatures frequently render active compounds completely inactive is a familiar fact, and records are not wanting to show that the same result may be produced at moderate temperatures, especially if chemical action ensues; isopropylphenylglycollic acid, for example, yields with concentrated hydrochloric acid at $20-45^\circ$ inactive iso-

propylphenylchloroacetic acid. The propriety of using hydrochloric acid as an etherifying agent for active acids, especially for hydroxy-acids, where it is often impossible to remove it by water before distilling the product, is therefore open to question, unless special precautions are taken to test the active ethereal salt for racemoid impurity. The same remark applies to the use of sulphuric acid. The method of preparation by the action of alkylic iodide on the silver salt, which has been very rarely used in the case of active acids, would seem, *a priori*, to be less open to objection; the action, so far as is known, is direct; it takes place at comparatively low temperatures, and no water is present. As a matter of fact we found that, in the case of the ethereal alkyl-oxy-succinates (*loc. cit.*), the method gave excellent results; a good yield of the ethereal salt was obtained, and no perceptible racemisation could be detected on recovery of the acid. Walker used the same method in preparing the active ethereal lactates, and found, as already stated, that it gave much more active products than those obtained by the direct action of acid and alcohol.

These results suggested to us the interesting question whether in general the reaction of a silver salt with an alkylic iodide yields more active products than the usual methods of etherification. We have, accordingly, prepared several of the ethereal malates by different processes, and find, as we expected, that the salts from silver malate are notably more active than the products obtained when hydrochloric acid or sulphuric acid is used as the etherifying agent. We have also prepared active ethylic lactate by similar methods, and have made further experiments with these preparations, as well as with the active malates, with the view of ascertaining, if possible, whether the difference of activity referred to is really due to racemisation or to some other cause.

Ethereal Malates and Acidyl Malates.

These compounds have been frequently investigated. Anschütz (*Ber.*, 1885, **18**, 1954) first showed how the ethereal malates could be obtained free from admixture with the fumarates and chlorosuccinates by a modification of the method of etherification devised by himself and Amé Pictet. More recently, Anschütz and Reitter (*Zeit. physikal. Chem.*, 1895, **16**, 493) have published the results of an accurate examination of the optical activity of the first four ethereal malates and their acetyl derivatives; and Walden (*loc. cit.*) has prepared by the same method, and subjected to optical examination, a still more extended series of these compounds.

The malic acid used by us was procured from Kahlbaum. An estimation of silver in the silver salt gave 62.09 per cent. of silver,

the calculated percentage being 62.07. A solution, in dry acetone (from the bisulphite compound), containing 7.48 per cent. of the acid, showed the specific rotation -5.95 , a value which agrees closely with that found by Guye, namely, -5.8° (*Ann. Chim. Phys.*, 1892, [6], 25, 206), and also with that quoted recently by Nasini and Gennari (*Zeit. physikal. Chem.*, 1896, 19, 117) for a 20.77 per cent. solution in the same solvent, namely, -6.01° . In a second experiment, however, for which the acetone was more carefully dried by several rectifications with calcium chloride, we found a higher specific rotation, the result being as follows. $C = 6.9890$, $l = 4$, $t = 6^\circ$, $\alpha = -1.85^\circ$, $[\alpha]_D = -6.62^\circ$. The activity of an aqueous solution of the potassium salt, made by neutralising the acid with standard potassium hydroxide, was also determined, with the following result.

$$C = 6.8618; l = 4; t = 11^\circ; \alpha = -1.87^\circ; [\alpha]_D = -6.81^\circ.$$

The specific rotation of the salt, calculated by interpolation for the same concentration from Schneider's results (*Annalen*, 1881, 207, 257) is -7.0° .

In preparing the ethereal malates from the silver salt, dry silver malate was added, a small portion at a time, to an excess of alkylic iodide. The action, which proceeded in some cases spontaneously, was completed by heating the mixture for a short time on the water-bath. The liquid having been diluted with dry ether, was filtered from the silver iodide, and distilled under reduced pressure. Except in the cases of the isopropyllic and isobutylic salts, as soon as the ether and alkylic iodide had passed over, the thermometer rose rapidly to the boiling point of the ethereal salt, which distilled within a range of 1° or 2° , leaving only a very small residue in the distilling flask. The yield of ethereal salt amounted to about 80 per cent. of the theoretical quantity calculated on the silver salt used, and in the preparation of the latter the loss of substance was found to be small. The ethereal salts were redistilled under reduced pressure until the variation in specific rotation was within the limits of observational error, which was found to be the case after the third or fourth distillation. The variation of activity on redistillation was slight, and as the change was in the upward direction, it may be concluded that racemisation did not occur in the process.

For purposes of comparison, ethylic malate was prepared also from the acid and alcohol, hydrochloric acid and sulphuric acid being used as the etherifying agent. In the former case, the method of Anschütz and Pictet was followed, with the slight modification that, after distilling off the excess of alcohol, dry potassium carbonate was added to the product until it was neutral; the liquid, after being diluted with dry ethylic ether, was filtered and distilled under reduced

pressure. It was found that by the use of potassium carbonate the liquid distilled almost constantly at once, and that a smaller residue was left in the distilling flask. In preparing ethylic malate by the sulphuric acid method, malic acid was heated for four hours on the water-bath with four times its weight of ethylic alcohol, to which a tenth part by weight of sulphuric acid had been added. The mixture having been neutralised with potassium carbonate and allowed to stand 12 hours, was filtered, and freed as far as possible from excess of alcohol by heating on the water-bath; dry ethylic ether was then added, and the precipitated potassium salt having been filtered off, the liquid was distilled under reduced pressure. Ethylic fumarate could not be detected in the product.

The acidyl malates were prepared by dropping the ethereal malates into an excess of acid chloride at 50° , and distilling the product under reduced pressure.

The results of our observations on the ethereal salts prepared by these methods are given below.

Methylic Malate (Silver Malate Method).—B. p. 129° at 16 mm.; $t = 11^{\circ}$, $l = 1$, $\alpha = -9.10^{\circ}$, $d_{11^{\circ}/4^{\circ}} = 1.2397$, $[\alpha]_D = -7.34^{\circ}$. The specific rotation on the previous distillation was -7.33° .

A second preparation gave a similar result, namely $\alpha = -9.25^{\circ}$ in the 100 mm. tube.

Analysis: Found C = 44.36, H = 6.38; calculated C = 44.44, H = 6.17 per cent.

Methylic Malate (Hydrochloric acid Method).—B. p. $130-135^{\circ}$ at 18 mm., $l = 1$, $\alpha = -8.17^{\circ}$.

Ethylic Malate (Silver Malate Method).—B. p. 138° at 25 mm.; $t = 11^{\circ}$, $l = 2$, $\alpha = -28.12^{\circ}$, $d_{11^{\circ}/4^{\circ}} = 1.1324$, $[\alpha]_D = -12.42^{\circ}$. The specific rotations in the two previous distillations were -12.34° and -12.33° respectively. The observed rotation at 19° in the 200 mm. tube was -27.90° , from which it will be seen that the activity does not alter very much between 11° and 19° .

A second preparation gave an approximately similar observed rotation, namely, $\alpha = -14.30^{\circ}$ in a 100 mm. tube.

Analysis: Found C = 50.39, H = 7.46; calculated C = 50.53, H = 7.37 per cent.

Ethylic Malate (Hydrochloric acid Method).—B. p. 131° at 15 mm.; $t = 11^{\circ}$, $l = 1$, $\alpha = -11.66^{\circ}$, $d_{11^{\circ}/4^{\circ}} = 1.1320$, $[\alpha]_D = -10.30^{\circ}$. Another portion of the same preparation, from which, however, the hydrochloric acid was not removed before distillation by the addition of potassium carbonate, had approximately the same activity, namely, -11.83° in the 100 mm. tube.

Analysis: Found C = 50.37, H = 7.52; calculated C = 50.53, H = 7.37 per cent.

A second preparation showed the rotation -11.58° .

Ethyllic Malate (Sulphuric acid Method).—B. p. 134° at 15 mm.; $t = 11^\circ$, $l = 2$, $\alpha = -23.52^\circ$, $d\ 11^\circ/4^\circ = 1.1339$, $[\alpha]_D = -10.37^\circ$.

Propyllic Malate (Silver Malate Method).—B. p. 147° at 10 mm.; $t = 11^\circ$, $l = 1$, $\alpha = -14.78^\circ$, $d\ 11^\circ/4^\circ = 1.0787$, $[\alpha]_D = 13.70$. The specific rotation on the previous distillation was -13.66° .

Analysis: Found C = 54.97, H = 8.43; calculated C = 55.05, H = 8.26 per cent.

Isopropyllic Malate.—We did not succeed in isolating this ethereal salt from the product of the action of isopropyllic iodide on silver malate. Our observations on the reaction are given below.

Normal Butyllic Malate (Silver Malate Method).—B. p. 170° at 15 mm.; $t = 11^\circ$, $l = 2$, $\alpha = -25.6^\circ$, $d\ 11^\circ/4^\circ = 1.0494$, $[\alpha]_D = -12.20$. The specific rotation on the previous distillation was -12.28° .

Analysis: Found C = 58.34, H = 9.12; calculated C = 58.54, H = 8.94.

Isobutyllic Malate.—The isobutyllic iodide acted vigorously on the silver malate, but as in the case of our preparation of isobutyllic alkyloxysuccinates by the same method, we failed to obtain a pure product. The liquid did not boil constantly, and a large residue of acid remained in the distilling flask; the distillate was optically active, but a crystalline deposit, probably fumaric acid, or maleic anhydride, separated from it on standing.

Ethyllic Acetylmalate, from Ethyllic Malate prepared from Silver Malate.—The ethyllic malate used was that described above, having the specific rotation -12.42° . The following were the observations made. B. p. $144-146^\circ$ at 19 mm.; $t = 12^\circ$, $l = 1$, $\alpha = -25.85^\circ$, $d\ 12^\circ/4^\circ = 1.1237$, $[\alpha]_D = -23.00$. The observed rotation on the previous distillation was $\alpha = -25.77^\circ$, from which it may be concluded that the activity of the compound is but little, if at all, impaired by heating to its boiling point. The activity increases rapidly with rise of temperature, differing in this respect from ethyllic malate; thus we found: at 5° , $\alpha = -25.40$; at 6° , $\alpha = -25.50$; at 12° , $\alpha = -25.85$; at 16° , $\alpha = -26.40$.

Analysis: Found C = 51.80, H = 7.16; calculated C = 51.72, H = 6.90 per cent.

Ethyllic Acetylmalate, from Ethyllic Malate prepared by the Hydrochloric acid Method.—The ethyllic malate used was the specimen already referred to, having the observed rotation $\alpha = -11.83^\circ$ in the 100 mm. tube at 11° . The following observations were made. B. p. 145° at 13 mm.; $t = 11^\circ$, $l = 1$, $\alpha = -24.25^\circ$, $d\ 11^\circ/4^\circ = 1.1238$, $[\alpha]_D = -21.58$.

Analysis: Found C = 51.59, H = 7.14; calculated C = 51.72, H = 6.90 per cent.

The same increase of activity with rise of temperature, referred to above, was also observed in the preparation. Thus at 5° the observed rotation was $\alpha = -23.87^\circ$.

Ethylic Butyrylmalate.—This salt was prepared from ethylic malate made from the silver salt, having the specific rotation -12.42° . As the reaction did not seem to take place at 50°, the butyryl chloride was heated to about 80° while the malate was added; the mixture was afterwards heated for a short time on the water bath. The results of our observations are as follows. B. p. 152–153° at 14 mm. $t = 11^\circ$, $l = 1$, $\alpha = -24.50^\circ$, $d_{11^\circ/4^\circ} = 1.0792$, $[\alpha]_D = -22.70^\circ$.

Analysis: Found C = 55.26, H = 7.87; calculated C = 55.38, H = 7.69 per cent.

Action of Isopropylic Iodide on Silver Malate.

The quantities of materials employed were 60 grams silver malate, and 100 grams isopropylic iodide. The action was very vigorous; as the liquid, after filtering off the silver iodide, was found to be strongly acid, it was treated with dry potassium carbonate before being distilled. On the third distillation, the product showed a constant boiling point, namely, 142° under a pressure of 27 mm., and the activity was unaltered. The specific rotation was found to be as follows. $t = 11^\circ$, $l = 1$, $\alpha = -34.90^\circ$, $d_{11^\circ/4^\circ} = 1.0257$, $[\alpha]_D = -34.03^\circ$.

It was evident from the very high activity of the product, amounting to two and a half times that of normal propylic malate, as well as from the relatively small yield of substance, that the reaction between the silver salt and the iodide had not proceeded in the normal manner. As it seemed possible that this unexpected result might be due to the violence of the action, or the influence of the potassium carbonate, which had not been used in the preparation of the other ethereal salts, a second experiment was made in which the isopropylic iodide was diluted with dry ethylic ether, and the addition of potassium carbonate omitted. The product boiled much less constantly than in the first experiment, owing, apparently, to the presence of free acid, and no attempt was made to purify the substance, but the same active compound was evidently formed, the observed rotation of the product being -31.70° in the 100 mm. tube. On repeating the preparation with the same quantities of material as were used in the first experiment, but leaving the product over dry potassium carbonate till it was neutral, 18 grams of a liquid were obtained, boiling constantly at 128° at 13 mm., and showing the following activity.

$t = 11^\circ$, $l = 2$, $\alpha = -61.95^\circ$, $d_{11^\circ/4^\circ} = 1.0347$, $[\alpha]_D = -29.94^\circ$. The results of the analysis of the first (I) and third (III) preparations were respectively as follows.

I. C = 57.35, H = 8.97; C = 57.04, H = 8.95 per cent.

III. C = 56.69, H = 8.89; C = 56.60, H = 8.73 per cent.

Isopropyl malate requires C = 55.05, H = 8.26 per cent.

The results of analysis and the varying rotations of different preparations show that the product is not a pure substance, in spite of its constant boiling point. A comparison of these observations with those on ethylic and normal propyl malates indicates that the mixture in question contains a compound much more optically active, and having a lower specific gravity and lower boiling point than isopropyl malate. From the product of hydrolysis with alcoholic potassium hydroxide, a lead salt was obtained, which was decomposed with sulphuretted hydrogen, and converted into the silver salt. An estimation of silver in the latter gave the theoretical result for silver malate, namely, 62.07 per cent. The highly active compound contained in the mixture referred to is, however, much more difficult to hydrolyse than the ethereal malates. Propyl malate is quickly hydrolysed when shaken with cold aqueous potassium hydroxide, but when the product obtained from the action of isopropyl iodide on silver malate is similarly treated, or even heated for some hours at 100° with aqueous alkali, a considerable quantity of an oil, showing a high activity, is left undissolved.

A comparative experiment was made by heating at 100° , in sealed tubes, equal weights of propyl malate and of the liquid obtained from the action of isopropyl iodide on silver malate, mixed with equal quantities of standard aqueous potassium hydroxide. In the latter case, a considerable proportion of the oil remained unhydrolysed, and by titration with standard acid, it was found that only about 75 per cent. of the alkali required for the hydrolysis of the propyl malate had been neutralised. An attempt was made to isolate the more active constituent by shaking the mixture with cold aqueous alkali. The unattacked oil was highly levorotatory, and amounted to about a fifth part of the substance taken. Estimations of silver in the silver salts prepared from the products of hydrolysis of the isopropyl compound with aqueous potassium hydroxide at 100° , and at the ordinary temperature gave, respectively, the following results: (1) 62.51, 62.55, (2) 61.81, per cent. The calculated percentage of silver malate is 62.07. From these results, it is probable that the product of the reaction of silver malate with isopropyl iodide is largely isopropyl malate contaminated with another much more active compound. The material at our disposal was insufficient for further examination, but we purpose investigating the reaction later.

Active Ethereal Lactates and Derivatives.

Klimenko (*J. Russ. Chem. Soc.*, 1880, **12**, 25—28) prepared ethylic *d*-lactate from silver sarcosylactate and ethylic iodide, and gave as its specific rotation $[\alpha]_D = -14.19^\circ$; he also prepared the substance by heating sarcosylactic acid with ethylic alcohol at 170° , but has not recorded the activity of the product. Le Bel (*Bull. Soc. Chim.*, 1893, [3], **9**, 674) obtained methylic *d*-lactate ($\alpha = -8.5^\circ$ in 100 mm. tube) by digesting sarcosylactic acid with methylic alcohol, and from this product prepared the acetyl and butyryl derivatives. Frankland and Henderson (*Proc. Chem. Soc.*, 1895, **11**, 54) have given the results of optical observations on methylic and ethylic *d*-lactates, methylic acetyl-*d*-lactate, and ethylic acetyl- and benzoyl-*d*-lactates; the material used was the *d*-lactic acid obtained by selective fermentation of ordinary lactic acid, and the ethereal lactates were made, we understand, by heating a mixture of the acid and alcohol. Walden (*Ber.*, 1895, **28**, 1293), in the course of his research on active chloro- and bromo-propionic acids, prepared ethylic *d*-lactate from sarcosylactic acid and alcohol by saturating the mixture with gaseous hydrogen chloride. Finally, J. Wallace Walker (*loc. cit.*) has prepared the active methylic, ethylic, and propylic lactates from active silver lactate, and also the corresponding ethereal salts of α -chloro- and α -bromo-propionic acids.

The material used in the preparation of the compounds examined by us was lævorotatory zinc ammonium *d*-lactate, obtained by the resolution of ordinary lactic acid by methods previously described (*Trans.*, 1893, **63**, 1143; 1895, **67**, 616). The zinc lactate prepared from this salt was found to lose, at 130° , 12.92 per cent. of water of crystallisation, the calculated percentage for active zinc lactate, which contains $2H_2O$, being 12.88; the salt was therefore practically free from racemoid compound.

Ethylic d-lactate (silver salt method).—Eighty-five grams silver lactate and 150 grams ethylic iodide gave only 22 grams of the ethereal salt, b. p. $69-70^\circ$, at 36 mm., $t = 14^\circ$, $l = 2$, $\alpha = -28.04^\circ$, $d_{14^\circ/4^\circ} = 1.0415$, $[\alpha]_D = -13.46^\circ$. Walker, using the same method, found the specific rotation -14.52° at 19° . The difference of the rotations can scarcely be accounted for by the difference of the temperature of observation, and it seems probable that in our preparation a certain amount of racemisation had occurred.

Ethylic d-lactate (sulphuric acid method).—A mixture of 30 grams of dextrolactic acid syrup, 120 grams of ethylic alcohol, and 12 grams of sulphuric acid was heated on the water bath for four hours, and then treated with dry potassium carbonate in quantity sufficient to neutralise the free acid and dry the ethereal salt. The liquid, after

being filtered and freed from alcohol by distillation, was treated with ethylic ether, again filtered, and finally distilled under reduced pressure. 15 grams of the ethereal salt were procured, boiling at $63-65^{\circ}$ at 25 mm. The following observations were made on the liquid after it had been distilled several times; b. p. 71° at 43 mm.; $t = 14^{\circ}$, $l = 1$, $\alpha = -10.77^{\circ}$, $d_{14^{\circ}/4^{\circ}} = 1.0423$, $[\alpha]_D = -10.33^{\circ}$.

Analysis: Found, C = 50.77, H = 8.68; calculated, C = 50.85, H = 8.47 per cent.

In a second preparation, the ethereal salt was obtained much more advantageously from zinc ammonium lactate by heating the dried salt with alcohol and sulphuric acid. The salt used gave the rotation $\alpha = -57'$, at 16° , in an 8 per cent. solution, and in a 200 mm. tube, and yielded zinc lactate containing the amount of water of crystallisation corresponding to $2H_2O$, namely, 12.88 per cent.; the material used was therefore pure lævorotatory salt. The mixture, consisting of 65 grams of dry zinc ammonium salt, 250 grams of ethylic alcohol, and 50 grams of sulphuric acid was heated on the water bath for four hours; the filtered liquid was neutralised with potassium carbonate, and then treated as described above. 39 grams of ethylic lactate were obtained, boiling at 65° under 27 mm. pressure, and having the observed rotation $\alpha = -11.05^{\circ}$, $l = 1$, $t = 14^{\circ}$. The product was therefore slightly more active than that described above.

Ethylic d-lactate (hydrochloric acid method).—Dextrolactic acid syrup was treated according to the method of Anschütz and Pictet. The product did not boil constantly, and the yield of ethereal salt was so small that it was impossible to purify it, but we were able to ascertain that it had approximately the same activity as the product obtained by the sulphuric acid method. The failure of the method was probably due to the presence of some calcium lactate in the lactic acid; the calcium chloride thus produced would combine with the ethereal salt.

Ethylic Acetyl-d-lactate from Ethylic d-lactate prepared by the Silver Salt Method.—Ethylic *d*-lactate ($[\alpha]_D = -13.46^{\circ}$) was treated with acetyl chloride, as already described in the case of the malates; b. p. $76-78^{\circ}$ at 15 mm.; $t = 14^{\circ}$, $l = 1$, $\alpha = -52.43^{\circ}$, $d_{14^{\circ}/4^{\circ}} = 1.0513$, $[\alpha]_D = -49.87^{\circ}$.

Ethylic Acetyl-d-lactate from Ethylic d-lactate prepared by the Sulphuric acid Method.—The ethylic *d*-lactate used was the specimen described above, $[\alpha]_D = -10.33^{\circ}$. Our observations were as follows: b. p. 81° at 18 mm.; $t = 14^{\circ}$, $l = 1$, $\alpha = -52.30^{\circ}$, $d_{14^{\circ}/4^{\circ}} = 1.0513$, $[\alpha]_D = -49.75^{\circ}$.

The specific rotation remained unaltered on re-distillation. This ethereal salt did not show the abnormal increase of observed rotation with rise of temperature exhibited by ethylic acetylmalate. The

observed rotations of one of the distillates in the 100 mm. tube at 6° and 14° were, respectively, -52.60° and -52.25° .

Deutro-ethylic Chloropropionate.—The ethylic lactate used was the specimen prepared by the sulphuric acid method, having the observed rotation $\alpha = -11.05^{\circ}$. 32 grams of ethylic lactate dissolved in 80 grams of chloroform were slowly added to 57 grams of phosphorus pentachloride, to which about 10 grams of chloroform had been added, the mixture being kept cool during the operation. The reaction took place readily, and all the phosphorus pentachloride dissolved on standing. Water having been added, the chloroform solution was separated, dried with ignited sodium sulphate, and distilled under reduced pressure. On the first distillation, under a pressure of 35 to 50 mm., three fractions were obtained, showing the appended observed rotations: under 64° , $\alpha = +10^{\circ}$; $64-80^{\circ}$, $\alpha = +18.5^{\circ}$; $80-140^{\circ}$, $\alpha = -3.6^{\circ}$. After several distillations, 12 grams of the chloropropionate were obtained, boiling at 68° (50 mm.), and showing the activity $t = 8^{\circ}$, $l = 1$, $\alpha = +19.41^{\circ}$. J. Wallace Walker found $\alpha = +21.21^{\circ}$ ($t = 11^{\circ}$) for a specimen prepared by acting on calcium lactate with phosphorus pentachloride, and $\alpha = +21.78^{\circ}$ ($t = 5^{\circ}$) for a specimen prepared similarly from lactic acid. The lower activity of our preparation may have been due to its not being entirely free from the oppositely active compound of high boiling point produced simultaneously with the chloropropionate, or to the presence of racemised substance.

Discussion of Results.

We tabulate, on the following page, the specific rotations of ethereal malates and acidylmalates examined by Anschütz and Reitter, Walden, and ourselves.

Columns I and II contain Anschütz and Reitter's, and Walden's results, respectively, obtained with ethereal salts prepared by Anschütz and Pictet's method of etherification, and with derivatives made from these; in column III are the results obtained by ourselves with the malates, prepared by the methods indicated, and with the ethylic acetyl- and butyryl-malates derived from them. We have also placed together, for comparison, Walker's observations and our own on the lactates and their derivatives.

The most notable feature in the numbers quoted for the malates is the higher activity of the ethereal salts prepared by the silver salt method as compared with that of the corresponding compounds obtained by the other methods. It is true that our observations were made at 11° , and Anschütz's and Walden's at 20° , but the large difference of activity exhibited cannot be due to this cause, as we found in the case of ethylic malate that the variations of activity

Ethereal Malates and Derivatives.

	I. A and R. [α] _D at 20°.	II. W. [α] _D at 20°.	III. P and W. [α] _D at 11°.			IV.
			Ag salt method.	HCl method.	H ₂ SO ₄ method.	
Methylic malate	- 6·883°	- 6·85°	- 7·34°	—	—	per cent.
Ethylic "	- 10·645	- 10·18	- 12·42	- 10·30°	- 10·37°	6·2
n-Propylic malate	- 11·601	- 11·62	- 13·70	—	—	14·3
n-Butylic "	- 10·722	—	- 12·20	—	—	15·3
Methylic acetylmalate	- 22·864	- 22·92	—	—	—	12·1
Ethylic "	- 22·601	- 22·52	- 23·00	- 21·58	—	—
n-Propylic "	- 22·675	- 22·85	—	—	—	—
n-Butylic "	- 19·925	—	—	—	—	—
Ethylic butyrylmalate	—	- 22·22	- 22·70	—	—	—

Ethereal Lactates and Derivatives.

	Walker [α] _D . Ag salt method.	P and W. [α] _D .	
		Ag salt method.	H ₂ SO ₄ method.
Ethylic lactate	- 14·52°	- 13·46°	- 10·33°
" acetylactate	—	- 49·87	- 49·75
" chloropropionate	{ α = + 21·21° α = + 21·78	—	α = + 19·41°

within short ranges of temperature were comparatively slight; besides this, observations made by ourselves at the same temperature on the ethereal salt prepared on the one hand from silver malate, and on the other by the hydrochloric and sulphuric acid methods, show the same striking differences. Neither are these due to differences in the activity of the malic acid used, as our substances were all made from the same sample of acid. The general correspondence of the results obtained by Anschütz, Walden, and ourselves in the case of ethylic malate, prepared by the hydrochloric acid method, indicate also that the malic acid used in all three cases was of nearly the same degree of activity. Assuming that the numbers obtained by us with the malates prepared by the silver salt method represent the actual specific rotations of the pure compounds, and that the lower activity of these salts when made by the other methods is due to racemisation, we have calculated the percentage of inactive racemised salt contained in the latter, using Anschütz's results for the purpose; these percentages are contained in column IV. It is, perhaps, worthy of remark that these numbers follow the same order as the specific rotations, the maximum 15·3 per cent., occurring at propylic malate, which is the most active of the series. The higher activity of the ethereal salts, prepared by the silver salt method, holds true also of the lactates; J. Wallace Walker has pointed out that the methylic and ethylic lactates which he prepared by this method are much more active than the compounds Le Bel, Frankland, and Henderson prepared by heating the acid and alcohol. The activity of the lactic acid used by Le Bel, and by Frankland and Henderson, is not quoted, and it seems probable from the low activity of the ethylic lactate ($[\alpha]_D = -8·6^\circ$), prepared by the latter, that their acid contained some racemoïd impurity to start with. To ascertain the difference of activity shown by lactates made from the same material by different methods, we prepared ethylic lactate by the silver salt method, and also by the sulphuric and hydrochloric acid methods, as already described. The activity $[\alpha]_D = -13·46^\circ$ of the lactate from the silver salt is not quite so high as that obtained by Walker ($14·52^\circ$) and by Klimenko ($14·19^\circ$) by the same method, the difference being due probably to some error in preparation on our part, but it is very much higher than the activity of the specimen prepared by the sulphuric acid method which had only the specific rotation $-10·33^\circ$. The difference of activity between our two ethylic lactates is in fact much greater than any differences found in the malates, amounting—if racemisation be assumed to be the cause—to 23·3 per cent. of racemoïd substance. We are inclined to think that similar differences will be found to exist generally in the case of the ethereal salts of hydroxy-acids, prepared by the silver salt and other methods,

and Mr. J. W. Rodger informs us that he has discovered such differences in the tartrates.

With the object of ascertaining whether the differences of activity referred to persist in derivatives of the ethereal salts made by the different methods, we prepared ethylic acetylmalate from the two different specimens of ethylic malate, and ethylic butyrylmalate from the more active ethylic malate; we also prepared ethylic acetyl lactate from both specimens of ethylic lactate, and ethylic chloropropionate from the less active ethylic lactate.

An inspection of the tabulated specific rotations will show that the activity of the derivatives is not proportional to that of the ethereal salts from which they were made; the differences exhibited by the original ethereal salts in fact almost disappear in the derivatives, or are much reduced. It will be seen, for example, that the specific rotations of the two specimens of ethylic acetyllactate are -49.87° and -49.75° , although the activity of the specimen of ethylic lactate, from which the latter of these was prepared, was 23 per cent. less than that of the specimen from which the former was made. Walden's ethylic malate, $[\alpha]_D = -10.18^\circ$, gave ethylic butyrylmalate, $[\alpha]_D = -22.22^\circ$; our ethylic malate from the silver salt, $[\alpha]_D = -12.42^\circ$, gave ethylic butyrylmalate, $[\alpha]_D = -22.70^\circ$, an activity much lower than that calculated from Walden's result even when allowance is made for the difference in the temperatures of observation. With respect to ethylic chloropropionate, this ethereal salt has not yet been prepared from ethylic lactate obtained from silver lactate, Walker having prepared his specimens from lactic acid and calcium lactate; it is, therefore, impossible to make a comparison between the activities of the chloropropionates prepared from the two ethylic lactates. If, however, we assume that Walker's specimens possessed the maximum activity corresponding to that of the substance derived from silver lactate, it will be seen that the activity of our chloropropionate, prepared from the less active ethylic lactate, considerably exceeds the activity calculated on this assumption. Thus the observed rotation of the less active ethylic lactate was $\alpha = -11.05^\circ$, that of the lactate from the silver salt -14.02° , that of Walker's chloropropionate $+21.78^\circ$; our chloropropionate should, therefore, have had the observed rotation $+17.17^\circ$. The rotation found was $+19.41^\circ$.

By the conversion of our chloropropionate into zinc lactate, which is described later, we found that it did actually contain racemised substance, which would account for it falling short of Walker's result.

It is very improbable that the difference in activity exhibited by the ethereal malates and lactates, prepared respectively from the silver

salts and by the hydrochloric or sulphuric acid methods, is due to foreign substances contained in them; the constancy of the boiling points, the results of analysis, and the comparative uniformity in optical properties shown by different preparations will scarcely admit of this explanation. The most obvious explanation, undoubtedly, is that the ethereal salts made with the aid of mineral acids undergo partial racemisation. The general agreement observable in the rotations of the ethereal malates, prepared by Anschütz and by Walden, and of our specimens of ethylic malate, prepared both with sulphuric and hydrochloric acid, shows that in spite of the varying conditions, the racemisation in each case must have occurred to the same extent. This would, no doubt, find an explanation in the conception of racemisation as a result of a reversible reaction, the velocity of which gradually diminishes until it proceeds so slowly that a practical equilibrium is established. Inasmuch, however, as the acetyl and butyryl derivatives show nearly the same rotation whether they are prepared from the more or less active malate, this explanation involves the further assumption that when an acidyl malate is prepared from the more active malate, a much greater amount of racemisation occurs under the action of the acidyl chloride, than when the same reaction is carried out with the less active malate, so that finally the same condition of equilibrium is reached in both cases. The same remark applies to the ethylic lactates and acetyl-lactates. We may here point out that on the hypothesis of racemisation, not only are the ordinarily accepted optical constants of the ethereal malates, and no doubt of other series of ethereal salts made with the aid of mineral acids, incorrect, but large corrections must also be applied to the values of the acidyl malates, and similar derivatives of hydroxy-acids, such as the tartrates, which have played a prominent part in the discussion of the relation of optical activity to chemical composition. Thus, for example, the rotations of the series of acetyl malates, quoted by Walden, do not exhibit any definite relation of optical activity to change of composition, but, assuming that our higher values for the malates made from the silver salt are the true values, and calculating the rotation of the acetyl malates from the latter, an entirely different result is obtained. It might then be concluded that the series shows a maximum of activity at the ethylic member.

	Observed (Walden).	Corrected values.
Methylic acetylmalate	-22.92°	24.56°
Ethylic " 	-22.52	27.51
<i>nor</i> -propylic acetylmalate. .	-22.85	26.94
<i>nor</i> -butylic " . .	-19.92 (Anschütz)	22.67

Similar corrections would have to be applied to the numerous other derivatives prepared by Walden.

The conclusion (based on the conception of racemisation as a reversible reaction) that the same condition of equilibrium is finally established in the case of the acidyl malates and lactates whether they are prepared from the more active or less active ethereal salt leads to the idea that the presence of racemoïd substance would protect the active substance from further racemisation. To test this we prepared ethylic lactate from a mixture of active and inactive zinc lactates by the sulphuric acid method. The salts were mixed in such quantities that the proportion of inactive acid present should be somewhat less than, according to our supposition, it is present in the ethylic lactate made by the same method from pure active material.

The proportions of active and inactive zinc lactate taken were such that the 83.4 and 16.6 per cent. of active and inactive lactic acid respectively were present. On the supposition that an equilibrium was established when 23.3 per cent. of inactive acid was present in the solution (as shown by the ratio between the specific rotations of the two ethereal salts, 13.46° and 10.33°), about 6.7 per cent. of the active acid would be racemised, and the ethereal salt produced should have the rotation $\alpha = -10.77^\circ$, that is, should be identical with the ethereal salt prepared from pure active material. The observed actual rotation of the ethereal salt thus prepared was $\alpha = -8.40^\circ$, which is slightly smaller than the rotation calculated on the assumption that the inactive substance added had no protective effect, namely, -8.98° . The idea, therefore, that a state of equilibrium between active and inactive substance is set up in the course of the reaction under consideration does not receive any support from this experiment.

With the view of detecting the presence of racemoïd substance in the ethylic malate ($[\alpha]_D = -10.30^\circ$) prepared by the hydrochloric acid method, we hydrolysed 15 grams of the ethereal salt with potassium hydroxide, obtained the lead salt by precipitation, and from this, in the usual manner, the acid. The dry acid was dissolved in acetone and filtered; the filtrate was then evaporated to dryness, and the residue left in a vacuum over sulphuric acid till constant in weight. The specific rotation of the recovered acid in acetone solution was determined as follows: $t = 5^\circ$, $l = 2$, $c = 6.8856$, $\alpha = -0.93^\circ$, $[\alpha]_D = -6.75^\circ$.

The activity of the original acid used under similar conditions was $[\alpha]_D = -6.62^\circ$. The experiment gives no indication of the presence of racemised acid, but the result can scarcely be regarded as decisive owing to possible error arising from the smallness of the rotation,

and to the risk of the inactive acid having been eliminated in the course of recovery. To avoid these possible sources of error, the experiment was modified as follows: 3 grams of each of the specimens of ethylic malate, prepared respectively from silver malate, and by the hydrochloric acid method and showing the rotations -14.30° and -11.66° , were carefully weighed, and, to each, 33 c.c. of standard potassium hydrate were slowly added, the quantity being slightly in excess of that required for complete hydrolysis. After standing some time, the solutions were each made up to 50 c.c., and examined in a 400 mm. tube at 5° . The readings were respectively -2.72° and -2.51° ; the solutions were then heated at 100° in tightly stoppered bottles in order to ensure the hydrolysis being complete in both cases, and they were found to have undergone no further change on examination with the polariscope. Of the two products of hydrolysis, that from the less active ethereal salt showed certainly the lower activity, but the difference was less than half what it should have been, if calculated from the relative rotations of the ethereal salts.

With the view of getting a more decisive result, we examined the specimens of ethylic lactate of lower and higher activity by hydrolysis, and conversion of the products into zinc lactate, in which the presence of inactive salt can be more certainly detected by the water of crystallisation than is possible in the case of the malates. 3 grams of ethylic lactate from the silver salt ($[\alpha]_D = -13.46^\circ$) were heated with 150 c.c. of water and excess of zinc carbonate for 14 hours on a water bath, using a reflux condenser. The liquid was then filtered and evaporated nearly to dryness, care being taken to keep the salt which separated, under the surface of the solution. An estimation of the water of crystallisation in the air-dried salt thus obtained, made by heating it at 125° till constant in weight, gave the result 13.19 per cent., the calculated percentage for pure active zinc lactate being 12.88. As the salt might well retain traces of free lactic acid or other volatile impurity, the object we had in view having precluded its recrystallisation, it may be concluded that the ethereal salt from which it was recovered contained little or no racemised substance. The same experiment was performed under the same conditions with ethylic lactate ($[\alpha]_D = -10.33^\circ$) prepared by the sulphuric acid method. 3.3 grams of air-dried salt were obtained, which was found to contain 13.38 per cent. of water of crystallisation. Calculating from the quantity of inactive substance contained in the ethereal salt, as indicated by the ratio of its activity to that of the ethereal salt prepared by the silver-salt method, the water of crystallisation should have been 14.11 per cent. Another similar hydrolysis was carried out with 5 grams of a specimen of ethylic lactate similar in activity to the last; two successive crops of

zinc lactate were obtained containing respectively 13.10 and 13.35 per cent. of water. The residue obtained from the mother liquor was slightly viscous, and could not be further examined; it was, moreover, so small that it is scarcely possible that it contained all the inactive salt which calculation led us to expect. A larger quantity, 15 grams, of ethylic lactate ($\alpha = -11.01^\circ$) was hydrolysed with barium hydroxide; the acid, having been liberated from this by the addition of rather less than the calculated quantity of sulphuric acid, the solution was filtered, treated with zinc carbonate, again filtered, and the solution of zinc lactate evaporated as nearly to dryness as the risk of the salt losing its water of crystallisation would allow; the salt thus obtained was dissolved in water, and two successive crops of crystals from the solution were found to contain respectively 13.17 and 13.20 per cent. of water of crystallisation. An estimation of zinc in the anhydrous salt gave the number 26.79, the calculated percentage being 26.87. The united mother liquors were evaporated nearly to dryness, but the residue containing a little undecomposed barium lactate, and being, moreover, very small in quantity, could not be further examined. The activity of one of the crops of zinc lactate was found to be as follows: $t = 9^\circ$, $l = 4$, $c = 7.48$, $\alpha = -1.87^\circ$, $[\alpha]_D = -6.25^\circ$. This result corresponds exactly with the specific rotation -6.29° previously found with the pure active zinc lactate (Trans., 1895, **67**, 623). These observations lead us to conclude that active ethylic lactate prepared by the sulphuric or hydrochloric acid methods may contain small quantities of racemised compound, but that the proportion of it present is too small to account for the low activity as compared with that of the product obtained from silver lactate.

Our failure to detect the expected amount of racemised compound in the ethereal malates or lactates prepared by the mineral acid methods of etherification, coupled with the remarkable fact of the comparatively constant activities obtained by different observers by these methods, and the fact that the ethereal salts thus prepared, and those prepared from the silver salts, yield acidyl derivatives of nearly the same degree of activity, have led us to entertain the idea, however improbable, that the ethereal salts of hydroxy-acids prepared by the two methods may possibly differ in constitution or configuration. The close agreement between the specific gravities of ethereal salts prepared by the different methods, it must be admitted, militates against this view, but, on the other hand, it may be concluded that the differences in specific gravity, if they existed, would be very slight, and very exact determinations would be required to detect them. Circumstances prevent us pursuing the investigation further together, but it will be continued by one of us.

Whatever may be the cause of the differences in optical activity of the ethereal salts of hydroxy-acids prepared by different methods, it is evident that until the matter has been further investigated it will be unsafe to base any conclusions regarding the relation of optical activity to chemical constitution on observations made on such substances.

Conversion of Dextrolactic into Lævolactic acid.

It has been already stated, that in order to ascertain if our specimen of ethylic chloropropionate, which had been prepared from the ethylic lactate of low activity, contained any inactive chloropropionate, we converted it into zinc lactate. The ethylic lactate referred to had been prepared from lævorotatory zinc ammonium lactate, and was itself lævorotatory. It has been shown by Walden and by J. Wallace Walker that when the hydroxyl of the ethereal lactates is replaced by chlorine or bromine, by the action of phosphorus chloride or bromide, the sign of activity is reversed. Our ethylic chloropropionate was dextrorotatory, as was expected, but on converting the compound back again into zinc lactate we found that the recovered salt had the opposite activity to that of the lactate with which we started. The same remarkable inversion had, in fact, occurred, which Walden (*Ber.*, 1896, **29**, 133) has recently observed in the case of malic acid. He has shown that each of the malic acids, under the action of phosphorus halides, yields an oppositely active halogen succinic acid, and that each of these in turn yields a malic acid of the same order of activity as itself, so that by the reactions indicated each of the optically active malic acids may be inverted. We find that the same phenomenon occurs in the case of dextrolactic acid, and will, no doubt, be exhibited also by its oppositely active isomeride.

We first attempted to reproduce lactic acid from the ethylic chloropropionate by the action of potassium hydroxide in excess. On gently warming the chloropropionate with aqueous alkali, the ethereal salt was apparently hydrolysed, but chlorine was not removed from it; on boiling, potassium chloride was quickly formed, but the resulting solution was inactive. Some of the ethereal salt was then warmed with water and silver oxide; as it remained apparently unaltered, enough potassium hydroxide was added to hydrolyse the compound in the expectation that the solution of the potassium salt might be acted on by the silver oxide. No chloride of silver seemed to be produced on warming, and the solution was found to be dextrorotatory. After boiling for 20 minutes, the solution still remained dextrorotatory, and much of the potassium chloropropionate remained unaltered, for, on testing a small portion of the solution by boiling with excess of potassium hydrate, potassium chloride was produced in

abundance. These attempts to effect the conversion into active lactic acid having failed, the rest of the ethylic chloropropionate, 8·7 grams, was dissolved in aqueous alcohol, and hydrolysed by adding to it slowly the calculated quantity of barium hydrate dissolved in 100 c.c. of warm water. The solution was neutral, and was found to have a slight lævorotation, from which it appears that the activity of barium chloropropionate is in the opposite sense to that of the acid. The chloropropionic acid was liberated by adding the calculated quantity of sulphuric acid. To the filtered solution of the acid, which was dextrorotatory, rather more than the quantity of silver oxide required to form the silver salt was added; silver chloride was formed in abundance on warming the solution on the water bath, and the solution became very acid. The completion of the reaction was ascertained by boiling some of the filtered solution with excess of potassium hydroxide and finding that no more chloride was produced. The filtered solution was next saturated with sulphuretted hydrogen, again filtered, and then concentrated by evaporation. The solution of lactic acid thus obtained was lævorotatory, and on neutralising it with zinc carbonate the rotation was reversed. The deposit of crystalline zinc salt obtained from the concentrated solution, after being recrystallised and dried at 130° , was found to contain 26·90 per cent. of zinc; the calculated percentage for anhydrous zinc lactate is 26·87. The water of crystallisation in the salt was 14·01 per cent., the calculated percentage for $2\text{H}_2\text{O}$ being 12·88. The salt, therefore, contained a considerable amount of inactive zinc lactate, a result which was to be expected from the observed activity of the ethylic chloropropionate from which it was recovered. The presence of the inactive salt was also borne out by the specific rotation, a determination of which gave the following result: $t = 8^{\circ}$, $l = 4^{\circ}$, $c = 7\cdot48^{\circ}$, $\alpha = +1\cdot72^{\circ}$, hence $[\alpha]_D = +5\cdot75^{\circ}$. The specific rotation of the pure active salt, under similar conditions, is $+6\cdot29^{\circ}$. The chief part of the racemisation probably occurred during the production of the ethylic chloropropionate from ethylic lactate, for the zinc lactate from the latter contained, as has already been shown, much less racemised salt. Lactic acid was set free from the inverted zinc salt by sulphuretted hydrogen, and its solution was found to be lævorotatory.

The remarkable inversion of optical activity, discovered by Walden, of which we have furnished another illustration, seems at first sight inexplicable by the current theory of the asymmetric carbon atom. Armstrong (*Proc. Chem. Soc.*, 1896, 45) has, however, offered a simple and ingenious explanation of the apparent anomaly which quite accords with the ordinarily accepted views. He supposes that by the action of phosphorus pentachloride on a hydroxy-acid, an intermediate compound containing the complex $\text{C} \begin{smallmatrix} \text{O} \\ | \\ < \\ | \\ \text{PCl}_3 \end{smallmatrix}$, may be formed,

which, by the action of hydrochloric acid is resolved into a chloro-acid and phosphorus oxychloride, and points out that if in this reaction "the attack became *directed* by the phosphorus, so that the chlorine took up the position of the phosphorus, complete inversion would be effected."

Walker found, in preparing the active ethereal halogen-propionates from lactic acid, that a small yield of the ethereal salt was obtained, and that in each case a large quantity of a high boiling compound was produced, which contained phosphorus, and was strongly active in the sense opposite to that of the propionate. We had a similar experience in preparing ethylic chloropropionate from lævorotatory ethylic lactate. The fraction of oil boiling above 80° gave, as already stated, a rotation of -3.67° in the 100-mm. tube. The oil went rapidly into solution on boiling with water, and on neutralising this solution by adding zinc carbonate, much zinc phosphate was precipitated, which was separated by filtration. The zinc salt of the acid produced in the reaction was much more soluble in cold water than in hot, and was obtained in the crystalline state by warming the solution and filtering. Its solution in water was lævorotatory. The acid, obtained by decomposing the salt with sulphuretted hydrogen, was a syrup, and was strongly lævorotatory in aqueous solution. It contained phosphorus, as phosphoric acid was abundantly formed on boiling it with nitric acid. The action of phosphorus pentachloride on the active ethereal lactates will be further examined in order to ascertain if the bye-product referred to is of the nature suggested by Armstrong.

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LII.—*The Hydriodides of Hydroxylamine.*

By WYNDHAM R. DUNSTAN, F.R.S., and ERNEST GOULDING.

In a previous paper (Proc., 1894, 138), the authors showed that methylic iodide reacts at the ordinary temperature with excess of a solution of hydroxylamine in methylic alcohol, much heat being evolved. The solution of hydroxylamine is prepared by the interaction of molecular proportions of hydroxylamine hydrochloride and sodium methoxide dissolved in methylic alcohol. On evaporation, a mixture of *hydriodide of trimethylhydroxylamine* and hydriodide of hydroxylamine crystallises out; these compounds are separated by dissolving in methylic alcohol and fractionally precipitating with ether. The hydriodide of hydroxylamine thus

obtained contains three molecular proportions of hydroxylamine combined with one molecular proportion of hydrogen iodide $(\text{NH}_2\cdot\text{OH})_3\cdot\text{HI}$. By further evaporation of the residual solution, we have isolated a second, and apparently definite, hydriodide containing two molecular proportions of hydroxylamine combined with one molecular proportion of hydrogen iodide $(\text{NH}_2\cdot\text{OH})_2\cdot\text{HI}$. The normal salt, $\text{NH}_2\cdot\text{OH}\cdot\text{HI}$, could not be found. The same hydroxylamine hydriodides are produced by the interaction of hydroxylamine and ethylic iodide.

Both the salts are well crystallised and comparatively stable, especially the trihydroxylamine compound. They have since been obtained by the direct combination of hydroxylamine (dissolved in methylic alcohol) and hydrogen iodide (dissolved in a little water); after evaporation, one or other salt or a mixture of the two, depending on the proportion of hydroxylamine used, crystallises out. We have not succeeded in crystallising any other definite hydriodide of hydroxylamine, and it is remarkable, especially in view of the stability of the normal hydrochloride, that no method we have tried, either direct or indirect, has furnished a crystalline normal hydriodide, $\text{NH}_2\cdot\text{OH}\cdot\text{HI}$. When a solution of hydroxylamine in methylic alcohol is mixed with the calculated quantity of aqueous hydrogen iodide to form this salt, the solution quickly darkens in colour from the liberation of iodine, and when evaporated, either by heating or by exposing it in a desiccator over sulphuric acid, further decomposition occurs. Decomposition, under various conditions, of hydroxylamine hydrosulphate, $(\text{NH}_2\cdot\text{OH})_2\cdot\text{H}_2\text{SO}_4$, with calcium iodide, barium iodide, or potassium iodide did not lead to the isolation of the normal compound.

Trihydroxylamine hydriodide, $(\text{NH}_2\cdot\text{OH})_3\cdot\text{HI}$, forms thin, crystalline plates which do not undergo any change in dry air, but in moist air gradually deliquesce, losing hydroxylamine. It is soluble in water and in methylic and ethylic alcohols, but not in ether; if this salt is recrystallised, either from hot methylic alcohol or especially from water, it gradually loses hydroxylamine, passing by degrees into the dihydroxylamine compound, which accounts for the higher percentages of iodine found in the analyses of certain specimens recorded below; but this loss does not occur if a little free hydroxylamine is present in the liquid. The salt is acid to litmus paper, and behaves as a powerful reducing agent. When gently heated in the dry state, it suddenly decomposes in the neighbourhood of 100° , nitrogen and water being evolved and ammonium iodide left as a residue. We find that the amounts of these products are formed in accordance with the equation $(\text{NH}_2\cdot\text{OH})_3\cdot\text{HI} = \text{NH}_4\text{I} + \text{N}_2 + 3\text{H}_2\text{O}$. Various specimens of the salt have been

analysed, the iodine being estimated in the usual manner as silver iodide, and the hydroxylamine by titrating the aqueous solution with standard iodine in the presence of magnesia.

I. $\text{NH}_3\text{O} = 41.03$ per cent.; $\text{I} = 58.5$ per cent.

II. $\text{NH}_3\text{O} = 41.1$ per cent.; $\text{I} = 58.4$ per cent.

III. $\text{NH}_3\text{O} = 43.7$ per cent.; $\text{I} = 55.7$ per cent.

IV. $\text{NH}_3\text{O} = 43.59$ per cent.

V. $\text{NH}_3\text{O} = 43.8$ per cent.

Calculated for $(\text{NH}_3\text{O})_3\text{HI}$; $\text{NH}_3\text{O} = 43.6$, $\text{I} = 55.9$ per cent.

Specimen III was recrystallised from water in the presence of an excess of hydroxylamine; specimens I and II were recrystallised from methylic alcohol, and specimens IV and V from the same solvent in the presence of a slight excess of hydroxylamine.

Dihydroxylamine Hydriodide, $(\text{NH}_2\cdot\text{OH})_2\text{HI}$, is formed when the proper proportion of hydrogen iodide (in water) is mixed with a very slight excess of hydroxylamine (in methylic alcohol), or it may be obtained by evaporating the mother liquor from the trihydroxylamine salt. The crystals, which resemble in appearance those of the trihydroxylamine compound, deliquesce more quickly in moist air. When recrystallised from water, iodine is liberated. The salt is acid to litmus paper, and acts as a powerful reducing agent. It is more soluble in water and in methylic and ethylic alcohols than the trihydroxylamine compound, and, like this substance, is insoluble in ether. It is best crystallised from its solution in hot methylic alcohol, although even in this case some of the salt is decomposed. Different specimens were analysed with the following results.

I. $\text{NH}_3\text{O} = 34.5$ per cent.

II. $\text{NH}_3\text{O} = 33.9$ per cent.; $\text{I} = 66.7$ per cent.

III. $\text{NH}_3\text{O} = 33.4$ per cent.

Calculated for $(\text{NH}_3\text{O})_2\text{HI}$; $\text{NH}_3\text{O} = 34.02$ per cent.; $\text{I} = 65.45$ p. c.

From a solution of the di- and trihydroxylamine salts in methylic alcohol, the trihydroxylamine compound crystallises out first, and in this way a partial separation of the two salts may be effected.

There seems to be no obvious explanation of the molecular association which hydroxylamine exhibits in these salts. It is interesting to note that one of us has already shown that the simplest known oxime, formaldoxime, CH_2NOH , also exhibits the peculiarity of forming salts of the same type, in which 3 mols. of the oxime are combined with 1 mol. of the halogen hydride, $(\text{CH}_2\text{NOH})_3\text{HCl}$, &c. (Dunstan and Bossi, Proc., 1894, 55). The instability of the normal hydroxylamine hydriodide as compared with hydroxylamine hydrochloride may be partly explained by the readiness with which hydrogen iodide reduces the single molecule of hydroxylamine to ammonia. In

the case of hydrogen chloride, besides the stable, normal salt of the formula, $\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$, Lössen (*Annalen*, 1871, **160**, 242) has described two other compounds, one, $(\text{NH}_2\cdot\text{OH})_2\cdot\text{HCl}$, corresponding with one of the hydriodides now described, the other of the formula $(\text{NH}_2\cdot\text{OH})_3\cdot\text{HCl}$. The latter salt, however, requires re-examination, since the evidence for its existence offered by Lössen does not appear conclusive. We have not been able to isolate the corresponding hydriodide.

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LIII.—*The Determination of the Composition of a
“White Sou” by a Method of Spectrographic Analysis.*

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A FRENCH coin, formerly known as a “white sou,” was given to me by my colleague Professor J. P. O'Reilly, Foreign Secretary of the Royal Irish Academy, with the information that such coins were at one time commonly in circulation in France, but had now become obsolete. It was supposed that they had been made during the Revolution of 1798, being hurriedly struck from any dies which came to hand, and from an alloy into which such suitable metals had entered as were most easily obtainable and readily appropriated, such as copper roofing, bronze cannon, and church bells. It was suggested to me that it probably contained silver. Its colour was that of pale gold, that is to say, of the precious metal in the natural state when it contains about half its weight of silver. It was curious that it did not ring, but this might have been accounted for by the edges being slightly cracked, the more probable reason, however, being the peculiar composition of the coin which occasioned its cracking.

As it was possessed of some historical interest, it became desirable that its composition should be ascertained without injuring it, and accordingly I resolved to make its analysis by the spectroscopic method, which may be more accurately described as spectrographic. The quantitative analysis by means of the spectrograph has been described by me in the *Phil. Trans.* (**175**, 49; also 325, 1884), and occasionally put into practice by executing analyses of the old brass coinage of James II and of silver coins of the reign of Edward I, Edward III, and Alexander of Scotland, which latter were found in a

bronze pot discovered in the foundations of a house in Aberdeen, and given to me by my friend Dr. Alexander Walker of that city.

In order to analyse the sou, it was fixed in a clip and submitted to the action of a condensed spark, and the spectrum of the alloy obtained from the rays of the spark was photographed.

The photographs obtained were compared with those of the pure metals, when the composition of the coin was found to be, by inspection of the photographs, that of an alloy of copper, zinc, lead, and iron.

The proportions of the constituents of the alloy were ascertained to be respectively between the extreme limits of

13·9 per cent. and 14·6 per cent. lead.

67·3 per cent. and 72·45 per cent. copper.

8·405 per cent. and 15·56 per cent. zinc.

0·888 per cent. and 0·85 per cent. iron.

There was neither tin, gold, nor silver present; it was in fact remarkably free from the latter precious metal.

In order more closely to approximate to the actual composition of the coin, three alloys were made and submitted to the spark. After photographs had been taken from their spectra, Mr. Ramage, Assistant Chemist in the Royal College of Science, Dublin, carefully analysed the alloy No. 3 by the ordinary methods, as this was the only one in which the lines in the spectra of each of the constituents corresponded with those in the spectra of the metals in the coin, both in the number and the length and strength of the lines.

The alloys made as required for comparison had a composition shown by the following figures

	(1).	(2).	(3).
Lead.....	13·94	14·64	13·93 per cent.
Copper.....	*67·34	72·45	72·35 „
Iron.....	0·888	0·85	0·85 „
Zinc.....	*15·56	*8·405	12·70 „
	<hr/> 97·728	<hr/> 96·345	<hr/> 99·83 „

It was easily seen by inspection that *67·34 per cent. was too low for copper, and *8·405 per cent. too low for zinc. The alloy No. 3, in fact, was that which corresponded most closely and almost exactly with the composition of the coin. The zinc in No. 1 was undoubtedly too high, while the lead was practically correct. The iron in Nos. 2 and 3 was correct. The composition of the white sou is thus seen to be that of brass in which lead takes the place of one half the zinc. A sample of brass analysed in my laboratory gave the following figures: lead 0·4, copper 68·59, iron 0·72, and zinc 30·18 per cent.

It was considered that there would be no adequate advantage gained by filing or cutting the coin for the purpose of submitting the fragments to further analysis in the usual way.

As all kinds of antique jewellery and coins may be analysed satisfactorily by the spectrographic method without causing any injury, it seems desirable that this method should be more generally known and more frequently practised than at present.

LIV.—*On the Temperature of Certain Flames.*

By W. NOEL HARTLEY, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

HAVING, for some years past, given much attention to flames and the nature of the spectra they emit, I have endeavoured to ascertain, as far as practicable, the temperatures they were capable of attaining. Unfortunately no thermometer or pyrometer, even of the nature of H. Le Chatelier's thermoelectric couple, is suitable, because the mass of the material to be heated is too large, and in the use of the latter instrument its destruction would be involved in the measurements attempted.* It is impossible to measure with accuracy the *maximum* temperature of any part of a flame of small dimensions, because if a body is placed within the flame it must necessarily reduce its temperature.

I have elsewhere mentioned the fact that a candle flame is hot enough to melt platinum, if the material to be melted be only small enough to be surrounded by the heated gases, and not large enough to conduct the heat away. ("Oxy-hydrogen Blow-pipe Spectra." Part I. *Phil. Trans.*, 185, 161—212.)

From recent publications and discussions I imagine there must be some misconceptions prevalent as to the temperature of flames.

In this connection, I may quote Sir Humphrey Davy, "The real temperature of visible flame is perhaps as high as any we are acquainted with. Mr. Tennant was in the habit of showing an experiment, which demonstrates the intensity of its heat. He used to fuse a filament of platinum in the flame of a common candle; and it is proved by many facts that a stream of air may be made to render a metallic body white hot, yet not itself be luminous." (*Phil. Trans.*, 1816, 117.) "Flame is gaseous matter heated so highly as to be luminous, and to a degree of temperature beyond the white heat of solid bodies, as is shown by the circumstance, that air not lumi-

* Professor Vivian Lewes has used this form of pyrometer with wires of very small dimensions for measuring the temperature of flames.

nous will communicate this degree of heat. This is proved by the simple experiment of holding a fine wire of platinum about $1/20$ th of an inch from the exterior of the middle of the flame of a spirit lamp, and concealing the flame by an opaque body, the wire will become white hot in a space where there is not visible light." (*Phil. Trans.*, 1817, 68.)

Evidence of the High Temperature of a Candle Flame.—That combustion in a candle flame is productive of a very high temperature is capable of proof in various ways.

1st. Pure gold leaf melts with extreme ease in any part of a candle flame where there is complete combustion, from the point where the wick curls over, or just under the tip of the curl, up to the apex of the flame. The highest temperature is about halfway up near the zone of greatest luminosity, and either within or near to the mantle. Hence the temperature at the lowest computation cannot be less than 1045° C. at these positions. This experiment is not open to the objection that the gold combines with carbon contained in the flame, and that by such change its melting point is lowered, for this is not the fact.

2nd. Faraday has described how he melted platinum wires $1/3000$ th of an inch in diameter in a candle flame. (*Lectures on the Chemistry of a Candle*, 195. C. Griffin and Co., 1865.) I have myself melted fine wires of platinum in a candle flame, and the melting point of this element cannot be less than 1775° C. (Violle).

It has been remarked that a possible fallacy may underlie the deductions drawn from the behaviour of a platinum wire in a flame containing free carbon or carbonic oxide, on account of the specific chemical action which these substances may exert on the metal. (*Proc. Chem. Soc.*, 16th January, 1896, 5.)

While fully recognising the propriety of drawing attention to this matter, it is right to say that I can find no evidence of the melting point of platinum being lowered by the action of carbon, and according to my experience it is not materially altered.

3rd. The most striking evidence of the very high temperature even of a candle flame is obtained by a careful examination of the spectra which can be observed in it. The line spectrum of sodium which is caused by the dissociation of its oxide may usually be seen, and the spectrum of calcium oxide may be obtained by putting a trace of lime on the wick. But by far the most convincing proof of the very high temperature of the flame is the well known fact that the spectrum of carbon is always visible in the mantle. The two groups of bands in the yellowish-green, with wave-lengths about 5627 to 5372, and 5170 to 5086, are particularly brilliant, and also the group in the blue, wave-length from 4743 to 4688. Any flame

showing these bands, which belong to the vapour of carbon, and which can show the radiations characteristic of the vapour of calcium oxide, must be at a temperature approaching that of the oxy-hydrogen flame.

Proof that the Melting Point of Platinum is not materially Reduced by Carbon in the Flame.—In order to ascertain whether heating a platinum wire in a flame containing free carbon gives rise to the formation of a compound of platinum and carbon which melts at a lower temperature than pure platinum, the following experiments were made.

A length of about 17 inches of platinum wire was fixed to a support by means of a screw, the end of which nipped the wire; the opposite end was allowed to lie on a triangular file as a support, and through the wire a current of electricity was passed. The wire was then very gently drawn along the flat, horizontal surface of the triangular file until it was obvious that the metal was near its melting point. Then with increased caution the wire was shortened, but without exercising the slightest tension, until it grew hotter, and finally gave way by fusion.

The portion of the white-hot wire dropped immediately over the sharp edge of the file and was then squeezed down upon it to show exactly where contact was made, and the distance from this point to that end of the wire which had not been heated by the current was carefully measured. By deducting its length from the total length of the wire, the exact quantity which had been heated to melting point was ascertained. Some of the same wire was then heated for 10 or 15 minutes in a broad bat's-wing burner until it had lost its brightness. From time to time a coating of carbon could be seen upon it. This wire was then tried exactly in the same way; the results obtained being as follows.

Length of Wire heated to its Melting Point.

	I.	II.	III.
Pure platinum	$10\frac{1}{16}$ ths	$10\frac{2}{16}$ ths	10 inches.
Carbonised platinum..	$10\frac{9}{16}$ ths	$10\frac{4}{16}$ ths	10 „

It will thus appear that the melting point of the metal had not been altered.

That the current from the 15-storage cells decreased by use in the interval between the first and second pairs of experiments accounts for the reduced length of wire shown to have been heated, but inequalities in the wire and also increased accuracy in performing the experiment may also have had effect.

Thus the doubt that was cast upon the accuracy of Professor

Smithell's statement of the high temperature of the mantle of the Bunsen flame may be said to be dissipated.

The melting of platinum wires in a candle flame cannot be carried out with any ordinary wire. That which I used* was drawn by Wollaston's method—a core of platinum inside a tube of silver. The silver was dissolved away from several short lengths of wire by digesting it in strong nitric acid, in some instances, for a period of a week, until no more silver was removed, and the wires were then washed with distilled water until nothing further could be removed from them. They were invisible to the unaided eye, except when they were struck by a ray of sunlight. It is difficult to introduce more than very short lengths of wire into the flame, because the up-rush of heated gas or vapour carries the wire away with it. But, if held by two ends, the wire, though invisible, may be passed into the flame when it instantly melts.

I have made some experiments on other flames, all of which have a temperature as high as that of a candle. Platinum wire 1/1000th of an inch thick melts in any part of a hydrogen flame 1 inch in height; it melts in the inner cone of a cyanogen flame with extreme ease, also in the flame of carbon monoxide, when only 1 inch in height, if introduced into the inner cone of the flame, and with great ease if placed at the tip of the cone. It must be recollected, however, that a carbon monoxide flame 1 inch in height is of much larger volume than a candle flame of this height, because the gas does not ignite if allowed to flow under pressure from a narrow orifice. In this case the orifice was a platinum tube of 1/8th of an inch internal diameter. The temperatures thus recorded cannot have been lower than 1775° (Violle).

The latter experiment goes to confirm my calculation of the temperature of the Bessemer flame, based on the comparison of its spectrum with the spectra produced by the oxyhydrogen flame, and from the fact that the flame from a converter is the result of the combustion of carbon monoxide mixed with about twice its volume of nitrogen, the gaseous mixture burning in air with an initial temperature of about 1500° (*Phil. Trans.*, 185, 1041).

* Obtained from Messrs. Johnson and Matthey.

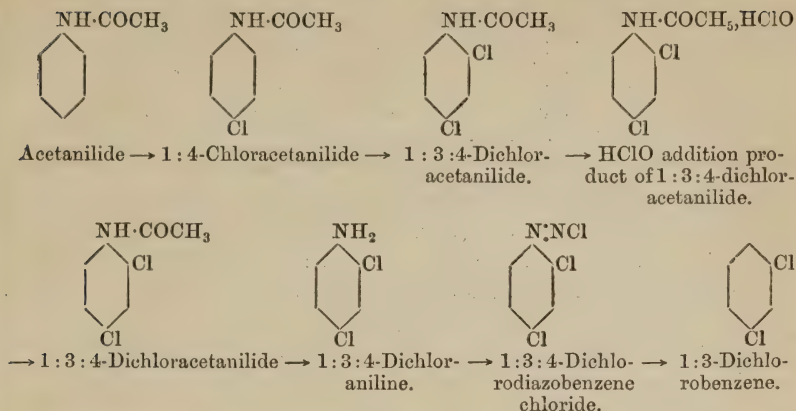
LV.—*Metadichlorobenzene.*

By FREDERICK D. CHATTAWAY, M.A., and R. C. T. EVANS.

METADICHLOROBENZENE, although well known, is extremely costly and difficult to procure, and no directions for preparing it in quantity are available. The authors, having required large quantities of this compound for an investigation of some derivatives of benzene on which they are engaged, have worked out a simple and very satisfactory method for obtaining it easily in bulk.

A large number of operations are needed, but the yields throughout are so good and so little affected by slight variations of condition that they think it worth describing, if only as an excellent preparation to put into the hands of students in order to illustrate several operations not frequently carried out in the laboratory. Körner's method of obtaining this compound from metanitraniline is not a practicable one, and, as is well known, the difficulty of obtaining it from metaphenylenediamine is great, for although Sandmeyer obtained 2 grams of metadichlorobenzene from 8 grams of metaphenylenediamine by adding sodium nitrite to a boiling solution containing cuprous chloride, the method, cannot be conveniently carried out on a large scale. Beilstein and Kurbatow's method is better, but treating acetanilide with chlorine, and diazotising with ethyl nitrite, are not at all satisfactory.

In the method employed by the authors, acetanilide dissolved in hot acetic acid is treated with a thin paste of bleaching powder until two hydrogen atoms occupying the meta-positions with respect to one another, are replaced successively by chlorine and a heavy liquid additive product of hypochlorous acid with the 1 : 3 : 4-dichloroacetanilide is formed. On cooling, this sinks, is readily separated, and when treated with hot alcohol rapidly decomposes, 1 : 3 : 4-dichloroacetanilide crystallising out. The dichloroacetanilide is then heated with strong sulphuric acid, which hydrolyses it, and on pouring the solution on to ice, 1 : 3 : 4-dichloraniline separates. The dichloraniline dissolved in a large quantity of alcohol is then mixed with an excess of hydrochloric acid, and diazotised by sodium nitrite; as the temperature rises during the interaction, the diazo-group first formed is replaced by hydrogen. The yield of 1 : 3 : 4-dichloraniline is nearly quantitative, and that of pure metadichlorobenzene over 50 per cent. of the weight of acetanilide taken. The following are the various steps in the preparation.



Preparation of the Hypochlorous acid Additive Compound of 1 : 3 : 4-Dichloracetanilide, $C_6H_3Cl_2 \cdot NH \cdot COCH_3, HClO$.—Acetanilide is dissolved in from 15 to 20 times its weight of dilute acetic acid (ordinary commercial acid containing about 30 per cent. of acetic acid), and although the exact amount of acid is immaterial, it is best to have a considerable excess present; the solution is heated in a large porcelain basin to about 80° , and good bleaching powder rubbed up to a thick cream with water is slowly added, the mixture being continually stirred; 1 : 4-chloracetanilide separates, and if the operation be stopped after the calculated quantity of bleaching powder has been used, a theoretical yield of this derivative can be obtained. As more bleaching powder is added, the 1 : 4-chloracetanilide is converted into 1 : 3 : 4-dichloracetanilide, and if the proper amount of bleaching powder be employed the latter can be also obtained nearly pure. On account, however, of some difficulty in knowing exactly when the conversion is complete and still more the trouble in collecting the precipitated anilide which clogs up the filter, it is more convenient to convert the anilide into the heavy, oily hypochlorous acid additive product by the addition of more bleaching powder, as, after subsidence, the supernatant liquid can readily be poured off from the oil. As the cream of bleaching powder is added to the hot, pulpy mass, each addition causes a frothing which keeps the mass stirred, the end of the reaction being shown by a free evolution of chlorine, very little escaping up to this point if the bleaching powder be carefully added.

After standing for an hour or so to settle and partially cool, the supernatant liquid is decanted, while still tepid, from the heavy, oily additive product; this is a heavy, yellowish oil of a peculiar odour, which, on standing, slowly decomposes, depositing crystals of pure 1 : 3 : 4-dichloracetanilide. This decomposition is accelerated if the

oil is dissolved in ether, and takes place very rapidly if it is treated with concentrated hydrochloric acid or warmed with alcohol; alcohol, however, gives a much purer product, as with hydrochloric acid chlorine is evolved and tarry substances are formed.

Preparation of 1 : 3 : 4-Dichloracetanilide, $C_6H_3Cl_2 \cdot NH \cdot COCH_3$.—When the liquid additive product is dissolved in about twice its volume of alcohol in a large porcelain basin, the solution soon becomes heated, and, after a time, boils violently, aldehyde being evolved; when the action is at an end, and the mass cool, 1 : 3 : 4-dichloracetanilide is left as a crystalline mass soaked with the remainder of the alcohol. As thus obtained it is pure, one crystallisation from acetone, yielding it in large, brilliant, colourless crystals. The action may be accelerated at the commencement by heating on a water bath. If used for the preparation of dichloraniline it is only necessary to drain the crystalline mass on a filter pump, and wash once or twice with a little water.

Preparation of 1 : 3 : 4-Dichloraniline, $C_6H_3Cl_2 \cdot NH_2$.—The replacement of the acetyl group by hydrogen is best effected by strong sulphuric acid. The drained crystals of the dichloracetanilide are dissolved in about four times their weight of strong sulphuric acid in a porcelain dish, and the solution heated at 110 — 120° for about 20 minutes; after cooling somewhat, it is poured into a moderate excess of water containing lumps of ice when the dichloraniline crystallises out as a white pulp. The compound is very easily separated by a filter pump, and, after thoroughly draining, is ready for diazotising. If the dichloraniline be required absolutely colourless and pure, it can be readily obtained so by distilling it with superheated steam from a slightly alkaline liquid.

Diazotisation and Conversion of 1 : 3 : 4-Dichloraniline into 1 : 3-Dichlorobenzene.—One part of dichloraniline is dissolved in a large flask in about five parts of alcohol, to which two parts of concentrated hydrochloric acid have been added; the flask should not be more than one-third filled with the mixture. Rather more than the calculated quantity of sodium nitrite very finely powdered and stirred up with about two parts of alcohol is then added gradually with continual agitation, the flask being placed in a stream of cold water. The temperature of the liquid rises quickly as the nitrite is added, and each addition is followed by a rapid evolution of nitrogen. It is best not to allow the temperature to rise above 60 — 70° , but no precaution other than that of keeping the flask in a stream of cold water need be taken. When all the nitrite has been added, the mixture is allowed to stand a few hours, and then steam is blown through it; the 1 : 3-dichlorobenzene distils over with the alcohol, and remains dissolved in it, but is readily obtained on diluting the distil-

late with rather more than its own bulk of water. The alcohol can be recovered and used again. A small quantity of a black tar, solidifying on cooling to a black pitch, remains behind with the liquid in the distilling flask.

The metadichlorobenzene, which sinks as a heavy oil to the bottom of the diluted alcohol, is separated, dried over calcium chloride, and distilled. Practically the whole distils exactly at the boiling point of pure metadichlorobenzene.

About 200 grams of acetanilide is a convenient quantity to convert at a time, a larger amount being inconvenient to work with in an ordinary laboratory. By this method a yield of pure metadichlorobenzene amounting to over 50 per cent. of the weight of the acetanilide used is easily obtained.

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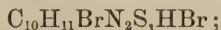
LVI.—*Halogen Additive Products of Substituted Thiosinamines.*

By AUGUSTUS E. DIXON, M.D.

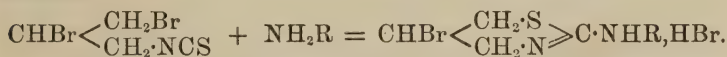
IN a paper communicated some years ago to this Society (Trans., 1892, 61, 545), I showed that dibromopropylthiocarbimide,



when brought into contact with aniline, affords not dibromopropylthiocarbamide, but a saline compound of the formula



the results of further investigation are embodied in a paper recently published (this vol., p. 17), in which it is shown that the thiocarbimide in question acts on ammonia and on primary or secondary bases, affording in each case the hydrobromide of a corresponding penthiazoline, the interaction occurring probably in accordance with the general scheme

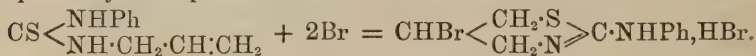


It has moreover been established in the latter communication that Maly's "thiosinamine dibromide," $\text{C}_4\text{H}_8\text{N}_2\text{S}\cdot\text{Br}_2$ (*Zeit. f. Chem.*, 1867, 42), obtained from bromine and allylthiourea, is identical with the product of the action of ammonia on dibromopropylthiocarbimide, and is accordingly the hydrobromide of a brominated penthiazoline.

From the latter result, it appeared probable that the same substituted penthiazolines as are obtained from the thiocarbimide and organic

bases would be formed on treating the corresponding substituted allylthiocarbamides with bromine; and some experiments in the direction indicated were therefore undertaken.

Allylphenylthiocarbamide was first tried, the alcoholic solution being mixed with bromine (diluted with chloroform) in the proportions required by the equation



Interaction at once took place, but not in the way expected; the mixture quickly became turbid, and on warming to expel the solvents, yellow masses of sulphur were deposited, and an oily basic liquid remained, from which, however, no penthiazoline could be extracted.

Substituting allylorthotolylthiocarbamide, the result was somewhat better; no sulphur was produced, and on evaporation a sticky oil was left, out of which solid matter gradually separated, apparently the wished for tolyl derivative in an impure condition, which was but little improved by repeated recrystallisation. As this orthotolyl compound had already proved difficult to isolate (*loc. cit.*, 28), the product was set aside until an experiment could be made, using allylparatolylthiocarbamide, a substance likely, judging from previous work on the para-base, to afford a more satisfactory result.

At this stage, however, the question of bromine addition was definitely settled by the appearance in the last issue of the Society's Journal of an abstract of a paper by Gadamer (*Arch. Pharm.*, 1895, **233**, 646—684), this chemist having directly obtained the brominated additive compounds of methylallyl-, dimethylallyl-, and (?) trimethylallylthiocarbamides respectively, by mixing their alcoholic solutions with bromine also dissolved in alcohol.

These substances appear to be regarded as merely additive compounds, but their recorded properties sufficiently resemble those of the penthiazoline derivatives above mentioned to leave practically no doubt that they are members of the latter class. "Methylallylthiocarbamide dibromide," for example, $\text{C}_5\text{H}_{10}\text{N}_2\text{S}, \text{Br}_2$, forms, according to Gadamer, large white crystals, very soluble in water, and melting at $145\text{--}146^\circ$. On treatment with silver chloride, it yields a "chlorobromide," readily soluble in water, which melts at $120\text{--}123^\circ$; moreover, it affords a *picrate* and an *aurochloride* (melting at 182° and 80° respectively), and a yellow *platinochloride*.

To make certain, the compound was prepared by slowly adding bromine (1 mol.) in chloroform to methylallylthiocarbamide (1 mol.) dissolved in alcohol and cooled by a freezing mixture. Union took place with great energy, and, on concentration, the product was obtained as a white, crystalline solid, which, after recrystallisation from moderately strong alcohol, melted at $145\text{--}146^\circ$, gave with picric

acid the yellow, crystalline picrate, and otherwise answered to the description of Gadamer's compound. The yield of recrystallised material was about 76 per cent. of the theoretical.

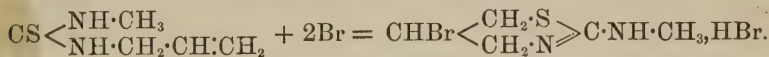
Some of the pure substance was dissolved in water, and the strongly acid solution mixed with excess of dilute caustic potash. A clear, almost colourless oil was at once deposited, but soon hardened; it was removed, well washed with water, and dissolved in hot, slightly diluted alcohol, from which, however, it separated as an oil, which did not solidify even when kept many days in a desiccator or under diminished pressure. The oil was nearly insoluble in water, slightly alkaline to test paper, had, especially when warm, a faint, rather unpleasant, basic odour, and was freely soluble in alcohol or acids. It contained bromine and sulphur, though withholding the latter from both alkaline lead and ammoniacal silver salts even on boiling. On examining the alkaline solution from which the organic base had been precipitated,* it was found to contain, in addition to a little base (which gradually separated from it on standing) much potassium bromide.

The oil was analysed for sulphur, with the following results.

0.1932 gave 0.2145 BaSO₄. S = 15.26.

C₅H₉BrN₂S requires S = 15.33,

Consequently the aqueous "dibromide" under the influence of dilute alkali loses half its bromine as hydrogen bromide, leaving a basic residue, C₅H₉N₂SBr, the latter being presumably μ -methyl- γ -bromopenthiiazoline, and the former its hydrobromide, which had been produced in the manner represented by the equation



The "chlorobromide" obtained from the "dibromide" by acting on it with silver chloride, was doubtless the hydrochloride of the brominated base, that is, C₅H₉N₂SBr, HCl. In order to obtain it, the base was treated with hydrochloric acid, in which it readily dissolved, and the solution concentrated on the water bath; the clear brown acid syrup which was left became tough on standing, but did not crystallise.

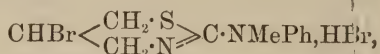
The methyl derivative, like several of the penthiazolines already mentioned, gave, on treatment of the alcoholic solution with (neutral or ammoniacal) silver nitrate, an insoluble silver compound, very sensitive even to dim daylight; the yellowish-white precipitate retains its colour if kept in the dark, but rapidly changes on exposure to actinic light, through mauve and reddish, to deep purple.

* 11.5 grams of "dibromide" afforded 7 grams of brominated base, equal to 84.3 per cent. of the theoretical.

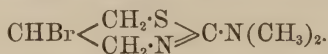
It remained to examine the action of dibromopropylthiocarbimide on methylamine.

The above constituents, in molecular proportion, were dissolved separately in alcohol, and the solution mixed, when, after a few seconds, a very vigorous action commenced, a portion of the contents being projected out of the vessel; on concentrating the residue and allowing it to stand, solid matter separated; this, when purified by recrystallisation and washing with alcohol, had the appearance and exhibited all the properties of the compound obtained by Gadamer from bromine and methylallylthiocarbamide, save that its melting point was not quite sharp (144—146°).

Secondary bases, as I have shown (*loc. cit.*), for instance, methylaniline and piperidine, also unite with dibromopropylthiocarbimide, affording disubstituted penthiazolines



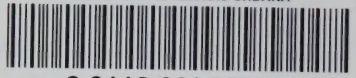
hence it may be safely concluded that Gadamer's dimethylallylthiocarbamide dibromide, and the chlorobromide which it gives with silver chloride, are the hydrobromide and hydrochloride respectively of the brominated base, μ -dimethyl- γ -brompenthiazoline,



Mention is made in the abstract above referred to of a *trimethylallylthiocarbamide* (from allylthiocarbimide and trimethylamine, at 150—160°) and its *dibromide*. If the former be really a thiocarbamide, its synthesis has a special interest, as being the only one of its kind hitherto effected. Allylthiocarbimide and triethylphosphine unite (Hofmann, *Ann.*, Suppl., 1, 47) to form a compound, $\text{C}_{10}\text{H}_{20}\text{NPS} = (?) (\text{C}_2\text{H}_5)_2\text{P}\cdot\text{CS}\cdot\text{N}(\text{C}_2\text{H}_5)(\text{C}_3\text{H}_5)$; but the only nitrogenous bases which have so far been combined with the thiocarbimides are those in which at least one typical hydrogen atom of the parent NH_3 is still retained.

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